Research review paper

Recent advances in two-phase partitioning bioreactors for the treatment of volatile organic compounds

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ABSTRACT

Biological processes are considered to be the most cost-effective technology for the off-gas treatment of volatile organic compounds (VOC) at low concentrations. Two-phase partitioning bioreactors (TPPBs) emerged in the early 1990s as innovative multiphase systems capable of overcoming some of the key limitations of traditional biological technologies such as the low mass transfer rates of hydrophobic VOCs and microbial inhibition at high VOC loading rates. Intensive research carried out in the last 5 years has helped to provide a better understanding of the mass transfer phenomena and VOC uptake mechanisms in TPPBs, which has significantly improved the VOC biodegradation processes utilizing this technology platform. This work presents an updated state-of-the-art review on the advances of TPPB technology for air pollution control. The most recent insights regarding non-aqueous phase (NAP) selection, microbiology, reactor design, mathematical modeling and case studies are critically reviewed and discussed. Finally, the key research issues required to move towards the development of efficient and stable full-scale VOC biodegradation processes in TPPBs are identified.

Contents

1. Introduction

Emission inventories have revealed that atmospheric pollutant emissions have continuously increased since the beginning of the 20th century, with volatile organic compounds (VOCs) representing about 7% of these emissions (Delhomenie and Heitz, 2005). Despite this low emission share, VOC emissions represent a major environmental and human health problem since most VOCs can be toxic depending on the concentration and exposure time and they also contribute to substantial damage to natural ecosystems (Delhomenie and Heitz, 2005; Hernandez et al., 2010; Muñoz et al., 2007). In addition, VOCs such as methane are greenhouse gases with high global warming potential (Rocha-Rios et al., 2009), while ozone formation is driven by the rapid photochemical oxidation of non-methane VOCs in the presence of nitrogen oxides (West and Fiore, 2005). Therefore, governments

Nomenclature

ALR	Airlift reactor
BC	Bubble column
BF	Biofilter
BTF	Biotrickling filter
C_i	VOC concentration (g m^{-3}) in the ith phase
C^*	VOC saturation concentration (g m^{-3})
EC	Elimination capacity (g m^{-3} h^{-1})
F	VOC mass transfer rate (g m^{-3} h^{-1})
$H_{i/j}$	VOC partition coefficient between ith and the jth phases (dimensionless)
k	Individual mass transfer coefficient (m h^{-1})
$\bar{K}_L a$	Overall volumetric mass transfer coefficient from the gas to the water/NAP phases (h^{-1})
$\bar{K}_L$	Overall mass transfer coefficient from the gas to the water/NAP phases (m h^{-1})
$k_L^{i/j} a$	Partial mass transfer coefficient between the ith and the jth phases (h^{-1})
K_s	Half-saturation constant of the Monod's growth model (g m^{-3})
P_G/V	Gassed power input (W m^{-3})
RE	Removal efficiency (%)
STR	Stirred tank reactor
TPPB	Two-phase partitioning bioreactor
VOC	Volatile organic compound

Greek symbols

ϕ	Volume fraction (dimensionless)
μ_{max}	Maximum specific growth rate of the microorganisms (h^{-1})

Subscripts

G	Gas
W	Water
NAP	Non-aqueous phase
mix	water/NAP mixture
TOT	Total

and environmental agencies strictly regulate these VOC emissions (Delhomenie and Heitz, 2005; Muñoz et al., 2007).

Among the available technologies for air pollution control, biological processes in many cases constitute the most cost-effective technology for treating VOC concentrations below about 5 g m^{-3} (Estrada et al., 2011; van Groenestijn and Lake, 1999). The stable and robust performance of biological systems for the treatment of a wide number of VOCs and odors has been consistently demonstrated, and their implementation at industrial scale is growing exponentially (Easter et al., 2005; Kennes and Thalasso, 1998). Biological techniques are based on the ability of microorganisms to convert VOCs into carbon dioxide, water and biomass under ambient conditions of temperature and pressure (Devinny et al., 1999; Lebrero et al., 2011). Unfortunately, biological processes perform poorly when the low transfer of hydrophobic VOCs from the gas phase to the microorganisms present in the aqueous phase limits microbial activity. As a consequence, low biodegradation performance has been recorded in biological systems treating hydrophobic VOCs such as hexane, ethane and styrene (Arriaga and Revah, 2005; Arriaga et al., 2006; Cesario et al., 1998; Dumont et al., 2006a; Hernandez et al., 2011a; Muñoz et al., 2006, 2007; Quijano et al., 2009a; van Groenestijn and Lake, 1999). Most authors agree on the fact that mass transfer limitations increase with VOC hydrophobicity as a result of the lower driving force

available for mass transfer. Fig. 1 shows a general VOC classification as a function of their Henry's law constant (H). Although this classification is arbitrary, it is useful to identify those VOCs whose biological removal is intrinsically limited by mass transfer as confirmed by empirical observations. In contrast to potentially low availability due to mass transfer limitations, microbial inhibition mediated by high VOC loading rates, load surges or by the accumulation of inhibitory metabolites can also cause the performance of biological processes to deteriorate (Nielsen et al., 2005; Yu et al., 2001).

Two-phase partitioning bioreactors (TPPBs) emerged in the early 1990s as innovative multiphase systems capable of overcoming two key limitations of traditional biological technologies for off-gas treatment: (i) the low VOC mass transfer from the gas phase to the microorganisms in the case of hydrophobic VOCs (Arriaga et al., 2006; Muñoz et al., 2007), and (ii) the microbial inhibition due to the presence of high VOC or toxic metabolite concentrations. TPPBs are based on the addition of a non-aqueous phase (NAP) with a high affinity for the target VOC into a biological process (Deziel et al., 1999; Kraakman et al., 2011), resulting in higher VOC absorption and driving forces for mass transfer (Clarke et al., 2006). Depending on the reactor configuration, the presence of a NAP may also improve the hydrodynamic behavior of the bioreactor, increasing both the gas/water and a gas/NAP interfacial area, which ultimately enhances the overall VOC mass transfer rates (Galindo et al., 2000; Quijano et al., 2010a). NAP addition can also buffer process microbiology against VOC loading surges and starvation periods by temporarily decreasing the VOC concentration in the aqueous phase or by acting as a VOC reservoir, respectively, which ultimately results in enhanced process robustness (Bailon et al., 2009; Hernandez et al., 2011b; Kraakman et al., 2011). Moreover, numerous studies have shown that most NAPs used in TPPBs also show a high affinity towards O$_2$ and consequently the O$_2$ mass transfer rate is also improved (Daugulis et al., 2011; Kraakman et al., 2011; Quijano et al., 2009b). Indeed, the affinity of some NAPs for O$_2$ is up to 10 times higher than that of water (e.g. the dimensionless H value for silicone oil and perfluorocarbons is 3.6 and 3.0, respectively, while H for water is 31.5). Therefore, the increase in the VOC mass transfer in TPPBs is concomitant with an increase in the O$_2$ transfer rate, enhancing opportunities for complete VOC mineralization. Consequently, the VOC biodegradation performance in TPPBs is often superior to that recorded in conventional biological systems (Montes et al., 2010; Muñoz et al., 2007).

The increased pace of research in the development of TPPBs for off-gas treatment conducted in the last 5 years has expanded our understanding of mass transfer phenomena and VOC uptake mechanisms, which constitute the fundamental processes governing the performance of these multiphase systems. Recent findings, such as the confinement of the biocatalytic activity exclusively in the liquid NAPs in some instances, have opened new possibilities for developing high-performance bioreactors. Additionally, better understanding of VOC uptake has recently confirmed the key role that microbiology plays on the performance of TPPBs, in spite of the fact that the microbiology has been usually considered to play a secondary role in TPPB optimization. This work constitutes an updated state-of-the-art review of TPPBs devoted to off-gas treatment. Recent findings and the challenges facing this technology to become a robust and cost-effective full-scale VOC treatment method are identified and discussed.

2. Process design

The performance of a TPPB fundamentally depends on (i) the selection of the NAP, (ii) the type of microbial community and (iii) the reactor configuration. The first studies on TPPB technology devoted to off-gas treatment were mainly focused on NAP selection. However, recent studies have shown that the type of microbial cells also plays a key role on the performance of TPPBs. On the other hand, the energy consumption required to disperse the NAP depends on the reactor
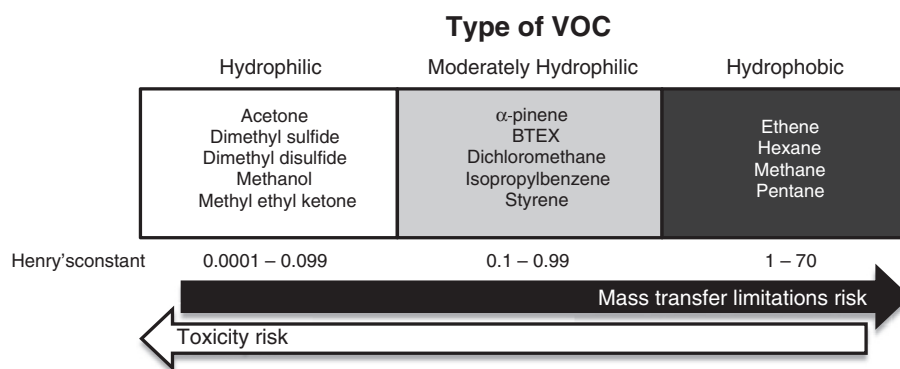
Type of VOC

Hydrophilic	Moderately Hydrophilic	Hydrophobic
Acetone Dimethyl sulfide Dimethyl disulfide Methanol Methyl ethyl ketone	α-pinene BTEX Dichloromethane Isopropylbenzene Styrene	Ethene Hexane Methane Pentane

Henry'sconstant 0.0001 – 0.099   0.1 – 0.99   1 – 70

Mass transfer limitations risk →

← Toxicity risk

Fig. 1. VOC classification in terms of their dimensionless Henry's law constant as well as their mass transfer limitation and toxicity risk to the microorganisms present in the biological treatment system (Henry's law constant values based on concentration ratios at 25 °C).

configuration, which finally impacts on the overall cost-to-benefit ratio of the process. These three fundamental issues are reviewed below.

2.1. NAP selection

The selection of the optimum NAP depends on the characteristics of the VOC to be treated, the VOC concentration, the reactor configuration and the characteristics of the microbial community present in the process (Quijano et al., 2009a). The pioneer, and still valid, list of NAP characteristics for TPPB implementation was first proposed by Bruce and Daugulis (1991) and includes a high affinity for the target VOC, biocompatibility, non-biodegradability and low cost. These authors also highlighted other important properties such as a low emulsion-forming tendency and availability in bulk quantities. Table 1 summarizes the commonly accepted characteristics that a NAP must fulfill for TPPB implementation in gas treatment processes (Darracq et al., 2010a; Muñoz et al., 2008; Quijano et al., 2010c).

Traditionally, liquid organic solvents such as n-hexadecane, perfluorocarbons or silicone oils (polydimethylsiloxanes) were used as NAPs due to the high diffusivity of the target substrates into these NAPs (Quijano et al., 2009a; Rocha-Rios et al., 2011). However, the use of n-hexadecane and other oils such as diethyl sebacate as NAPs for VOC treatment is hindered by their well-known biodegradability by many microorganisms (Arriaga et al., 2006; MacLeod and Daugulis, 2005; Quijano et al., 2010b). Similarly, the high volatility of perfluorocarbons together with their ozone depleting potential (Quijano et al., 2010c; Toft et al., 2006) discourages their use as a NAP in off-gas treatment applications. In this context, heptamethylnonane, despite being non-biodegradable, has been reported as being slightly volatile (Quijano et al., 2010c) and it is therefore not recommended as a NAP. Ionic liquids have been also studied as potential NAPs for VOC treatment; however, their use is still limited by their high cost, toxicity towards microbial cells and their high solubility

in water (up to 20 g L^{-1} for some imidazolium-based ionic liquids) (Brennecke and Maginn, 2001; Quijano et al., 2010d). In fact, recent investigations have shown that imidazolium ionic liquids might inhibit VOC biodegradation at levels as low as 5% (v/v) (Quijano et al., 2011). In contrast, Baumann et al. (2005) found that some phosphonium ionic liquids were biocompatible with *Pseudomonas putida*, *Achromobacter xylosoxidans*, or *Sphingomonas aromaticivorans*, which suggests that the potential of ionic liquids in TPPB implementation should be further investigated. Most authors agree on the fact that silicone oil is the only liquid NAP that fulfills all the expected characteristics listed in Table 1 (Arriaga et al., 2006; Darracq et al., 2010a; Dumont et al., 2011; Muñoz et al., 2006; Quijano et al., 2010c). In fact, silicone oil at percentages of 10–20 % (v/v) has been the most commonly used NAP in the last 5 years. Despite operational problems such as foaming and adhesion to reactor internals having been reported when using silicone oil as a NAP (Daugulis and Janikowski, 2002; Daugulis et al., 2011; Janikowski et al., 2002), recent studies have reported no foam production during hexane biodegradation when the microbial community was capable of growing immersed in the silicone oil (Hernandez et al., 2012; Muñoz et al., in press). Although the mechanisms involved in the inhibition of foam formation are still unknown, it can be hypothesized that the metabolites profile when the microorganisms grow immersed in the NAP was significantly different than that expressed when grown immersed in water. Such differences in the metabolites profile, including the potential inhibition of biosurfactant production, could be induced by the large differences in the amounts of VOC that silicone oil and water can dissolve (e.g. 4 orders of magnitude differences). Nevertheless, more research on this issue is needed to clarify this empirical finding.

Recently, solid inert polymers based on copolymers of polyurethane, vinyl acetate and ethylene (e.g., commercial trademarks Kraton, Elvax and Desmopan) have been tested as NAPs, gaining acceptance due to their low cost and facilitated separation and

Table 1
Characteristics to be fulfilled by a NAP for TPPB implementation.

Characteristic	Rationale	Reference
Biocompatible	Avoiding decreased metabolic activity.	Bruce and Daugulis, 1991
Non-biodegradable	Avoiding preferential NAP uptake over VOC biodegradation and NAP losses.	
High affinity for the target VOC	High VOC absorption in the TPPB.	
Non-hazardous	Avoiding toxic effects for operators and the environment.	
Low-emulsion forming tendency	Avoiding foaming and facilitating phase separation.	
Available in bulk quantities	Key characteristic for full scale applications.	
Low cost	Facilitating the implementation of a cost-effective process.	
Density different from that of water	Facilitating phase separation.	Cesario et al., 1992
Immiscible in water	Avoiding NAP losses and facilitating phase separation.	
Low vapor pressure	Avoiding NAP losses and release to the environment.	
Odorless	Avoiding unpleasant working conditions or even toxic effects to operators.	van Groenestijn and Lake, 1999
Good hydrodynamic characteristics	Allowing for good NAP dispersion and mass transfer performance. Related to the gas disruption capacity of the NAP.	Quijano et al., 2010a

recycling during VOC treatment (Daugulis et al., 2011; Morrish and Daugulis, 2008). Moreover, new polymer selection criteria based on a first principles approach for solid polymers including pollutant accessibility into the polymer, thermodynamic affinity and glass transition temperature have been recently reported by Parent et al. (2012). Table 2 summarizes the reported NAPs and the target VOCs in TPPBs devoted to gas treatment.

The high NAP affinity towards the target gaseous substrate, including oxygen, quantified through the dimensionless partition coefficient ($H_{G/NAP} = C_G \times C_{NAP}^{-1}$), has been considered to be a central requirement to be fulfilled (Daugulis, 2001; Muñoz et al., 2008). However, several studies have recently shown that NAP affinity was not always correlated with a high mass transfer performance in TPPBs. For instance, Littlejohns and Daugulis (2007) found a higher

Table 2
NAPs and target VOCs used in TPPBs devoted to off-gas treatment.

NAP	NAP characteristics	Target VOC	$H_{G/NAP}$ ($C_G\,C_{NAP}^{-1}$)	Reference
Silicone oil	Liquid polymer of dimethylsiloxane (kinematic viscosities from 5–200 cSt)	Oxygen	3.6	Quijano et al., 2010c
		Methane	2.0	Rocha-Rios et al., 2011
		Dimethyl sulfide	0.016	Darracq et al., 2010a
		Hexane	0.0058	Hernandez et al., 2010
		Dimethyl disulfide	0.00093	Darracq et al., 2010a
		Toluene	0.00064	Darracq et al., 2010a
		α-pinene	0.00018	Muñoz et al., 2008
		BTEX	–	Littlejohns and Daugulis, 2009
Hexadecane	Linear liquid alkane	Oxygen	6.6	Nielsen et al., 2003
				Dumont et al., 2006b
		Dimethyl sulfide	0.0088	Vuong et al., 2009
		Hexane	0.0040	Arriaga et al., 2006
		Toluene	0.0010	Boudreau and Daugulis, 2006
				Davidson and Daugulis, 2003a, 2003b
				Vuong et al., 2009
		Dimethyl disulfide	0.0007	Vuong et al., 2009
		α-pinene	0.000071	Muñoz et al., 2008
		Benzene	0.0020	Davidson and Daugulis, 2003a, 2003b
				Nielsen et al., 2005
				Nielsen et al., 2006
				Yeom and Daugulis, 2001
1-Octadecene	Long-chain alkene	Benzene	–	Yeom et al., 2000
FC40	Liquid perfluorocarbon	Oxygen	3.0	Quijano et al., 2010c
		Hexane	0.027	Hernandez et al., 2010
		Toluene	0.012	Cesario et al., 1997a
		α-pinene	0.0014	Muñoz et al., 2008
Diethyl sebacate	Liquid ester	Phenol	0.92	Guieysse et al., 2005
		Hexane	0.015	Arriaga et al., 2006
		α-pinene	0.000074	Muñoz et al., 2008
Heptamethylnonane	Liquid and highly branched alkane	Oxygen	3.4	Quijano et al., 2010c
		Methane	2.1	Rocha-Rios et al., 2011
		Hexane	0.0027	Hernandez et al., 2010
		α-pinene	0.000056	Muñoz et al., 2008
Heptamethyltrisiloxane	Liquid polyalkyleneoxide with three siloxane units	Hexane	0.0029	Hernandez et al., 2010
[C_4mim][PF_6]	Liquid imidazolium ionic liquid	Dimethyl sulfide	0.011	Quijano et al., 2011
		Dimethyl disulfide	0.0013	Quijano et al., 2011
		Toluene	0.00096	Quijano et al., 2011
[C_4mim][NTf_2]	Liquid imidazolium ionic liquid	Dimethyl disulfide	0.0012	Quijano et al., 2011
		Dimethyl sulfide	0.0090	Quijano et al., 2011
		Toluene	0.00061	Quijano et al., 2011
Rubber tires	Solid copolymer of polyisoprene, styrene-butadiene copolymer and polybutadiene	α-pinene	0.0005	Montes et al. 2011a
Kraton D4150K	Solid styrene/butadiene triblock copolymer	α-pinene	0.0003	Montes et al., 2011a
Kraton D1102K	Solid styrene/butadiene triblock copolymer	α-pinene	0.0004	Montes et al., 2011a
Kraton G1657	Solid styrene/butadiene triblock copolymer	Methane	4.0	Rocha-Rios et al., 2011
		Oxygen	3.0	Quijano et al., 2010c
		Hexane	0.0057	Hernandez et al., 2010
Pebax 2533	Solid polyether block amide	α-pinene	0.0009	Montes et al., 2011a
Hytrel G3548L	Solid copolymer of poly(butylene terephthalate) and polyether	α-pinene	0.0013	Montes et al., 2011a
Silicone rubber	Solid polymer of dimethylsiloxane	α-pinene	0.0007	Montes et al., 2011a
Silicone rubber	Solid polymer of dimethylsiloxane	BTEX	–	Littlejohns and Daugulis, 2009
Desmopan 9370A	Solid polyurethane of poly (oxytetramethylene) glycol and methyldiisocyanate	Methane	5.4	Rocha-Rios et al., 2011
		Oxygen	5.1	Quijano et al., 2010c
		Hexane	0.0168	Hernandez et al., 2010
Elvax 360	Solid poly(ethyleneco-vinyl acetate)	Oxygen	3.5	Quijano et al., 2010c
		Hexane	0.0135	Hernandez et al., 2010
Elvax 880	Solid poly(ethyleneco-vinyl acetate)	Methane	9.7	Rocha-Rios et al., 2011
ABA co-polymer	Solid styrene-butadiene co-polymer	Toluene	–	Daugulis and Boudreau, 2008

K_La for O_2 with glass beads than with silicone rubber beads, despite the fact that silicone rubber exhibits a higher affinity for oxygen. Likewise, Quijano et al. (2010a,c) found that NAPs with favorable hydrodynamic characteristics (e.g. good dispersion within the reactor or high bubble disruption capacity) showed higher O_2 mass transfer enhancements than those presenting a poor dispersion but higher affinity for O_2. These studies therefore confirmed that a high affinity for the NAP (equilibrium parameter) does not guarantee a high mass transfer performance in the TPPB. Moreover, the hydrodynamic behavior of the NAP must be carefully (and experimentally) considered during the selection process. General protocols for NAP selection can be found in the literature (Darracq et al., 2010a; Muñoz et al., 2008; Parent et al., 2012; Quijano et al., 2010c).

Solid polymers also exhibit a high affinity towards a variety of VOCs (Table 2). For instance, Kraton has $H_{G/NAP}$ values for α-pinene, hexane and methane that are in the same order of magnitude as those reported for silicone oil (0.0003, 0.0057 and 4.0, respectively). However, comparative studies on VOC biodegradation in the presence of solid and liquid NAPs clearly showed reduced removal performance under steady state conditions when solid NAPs were used. For instance, Hernandez et al. (2010) reported that hexane biodegradation in the presence of Kraton was similar to that recorded in a control reactor without the NAP, while the TPPB implemented with silicone oil supported a hexane biodegradation 2 times higher than that recorded in the control. Similarly, Hernandez et al. (2011b) found that mixtures of solid polymers (Hytrel, Zytel, Engage, recycled rubber tires, silicone rubber, Kraton) failed to increase the biodegradation performance of hexane, toluene and methyl ethyl ketone under steady state conditions compared to a control without the NAPs. These authors attributed the low performance of the solid NAP to its low interfacial area and to the wettability (or lyophobicity) of the polymer, which is a property that hinders direct hexane transfer from the gas to the NAP by promoting the repelling of the gas interface, (Rehmann et al., 2007; Ruthiya et al., 2003). This low performance may also be due to the low VOC diffusivity in the solid NAPs. Indeed, it has been reported that VOC diffusivity in solid NAPs can be up to 500 times lower than that in liquid NAPs (Montes et al., 2011a; Muñoz et al., 2008). However, it must be stressed that despite the lack of reports on VOC biodegradation improvement during steady operation arising from the use of solid NAPs, enhanced process stability against short term VOC surges has been demonstrated (Hernandez et al., 2011b). It can therefore be concluded that while liquid NAPs (e.g. silicone oil) seem to be able to increase VOC mass transfer and biodegradation under steady state conditions, solid polymers are advantageous as NAPs for VOC treatment only to increase process stability during transient operation. At this point it is important to note that Daugulis et al. (2011) recently pointed out the high cost of silicone oil as its main disadvantage as a NAP in TPPBs at full-scale. Nonetheless, these authors used high purity silicone oil (analytical grade for lab scale purposes) as a reference for comparison, while the cost of industrial grade silicone oil is actually ~55 times lower (3.6 € L^{-1}, VERKOL, Spain) and comparable to that of the solid NAPs. Nevertheless, the efficacy of this grade of bulk silicone oil must be experimentally assessed.

2.2. Microbiology

Recently, significant advances have been made in understanding the VOC uptake mechanisms in TPPBs, which has highlighted the relevance of microbiology on the performance of TPPBs. Both mixed and pure cultures have been used for gas treatment in TPPBs; however, most studies were performed with mixed cultures enriched from activated sludge or from soil (see Section 3). The preferential use of mixed cultures is likely due to the fact that microbial diversity often confers high resilience and robustness to biological gas treatment

systems (Briones and Raskin, 2003; Cabrol and Malhautier, 2011; Cabrol et al., 2011; Estrada et al., in press).

Conventional TPPB operation has generally considered that metabolic activity mainly occurs in the aqueous phase (Daugulis, 2001) and that the higher biodegradation performance of TPPBs over single-phase systems was based on (i) the establishment of a new gas/NAP/water mass transfer pathway (Kraakman et al., 2011) and (ii) the enhancement of the gas/water pathway (Quijano et al., 2010a). In this regard, the microorganisms used for VOC biodegradation in TPPBs were selected based on their ability to degrade a specific VOC or a mixture of VOCs and, to the best of our knowledge, no other microbial characteristics were considered. However, if a microorganism is able to grow immersed in a liquid NAP or at the water/NAP interface, all VOC concentration gradient available for the gas/NAP transfer pathway can be exploited as will be further discussed in Section 4.

The key role of microbial characteristics in multiphase systems was noted by Ascon-Cabrera and Lebeault (1993, 1995) who observed that approximately 50% of the total biomass adhered to the NAP/water interface during the biodegradation of chlorobenzenes and ethyl butyrate in a TPPB. The authors suggested that a direct substrate uptake from the NAP/water interface likely occurred. Later, MacLeod and Daugulis (2005) also found that the biodegradation of PAHs by *Mycobacterium* PYR-1 occurred exclusively at the NAP/water interface although the NAP in the process was indeed biodegradable. These interesting studies motivated subsequent investigations on substrate uptake in TPPBs devoted to off-gas treatment. For instance, Quijano et al. (2010e) proposed an experimental setup in which a pure culture of *Pseudomonas putida* aerobically degraded glucose in a TPPB operating with silicone oil. After a control period during which glucose was consumed, the sodium sulfite reaction with Co^{2+} at non-toxic concentrations was initiated in order to remove the oxygen from the aqueous phase for a short period of time. The authors reported that no glucose was consumed while sulfite depleted the oxygen concentration in the aqueous phase, concluding that oxygen uptake in the NAP did not occur. However, Hernandez et al. (2012) confirmed that hydrophobic microorganisms were able to grow immersed in silicone oil and take up both oxygen and hexane in the NAP. This system supported a hexane biodegradation performance 8 times higher than a similar TPPB operated with the same microorganisms dispersed in the aqueous phase (the microorganisms became completely hydrophobic within 48 h). A recent study conducted in our laboratory also showed that stable long-term biodegradation of hydrophobic VOCs can be obtained by using hydrophobic microorganisms confined within silicone oil (Muñoz et al., in press). In this study, despite the fact that microbial population changes (e.g. diversity, proportion of each strain, etc.) were not ruled out, the macroscopic behavior of the microorganisms (e.g. cell hydrophobicity) as well as VOC biodegradation performance remained stable. Thus, the selection of hydrophobic strains able to degrade a variety of hydrophobic VOCs inside the NAPs constitutes a research advance of paramount relevance towards the development of a new generation of high-performance TPPBs using liquid NAPs. In this regard, cell hydrophobicity (which has been shown to be an inducible property) must be considered as a key criterion to select effective microorganisms for TPPBs devoted to off-gas treatment (Hernandez and Muñoz, 2011).

At this point it must be stressed that TPPBs as a technology for biological gas treatment are basically open (non-sterile) systems that are intended to cope with fluctuating VOC loadings and pollutant compositions. Therefore, gradual changes in the microbial community structure are expected. Bailon et al. (2009) performed an interesting study examining the changes in the microbial populations of a TPPB degrading dichloromethane. The authors found that although the originally inoculated *Hyphomicrobium* strains were present, they were not dominant after long-term operation (250 days) and new

bacterial populations were detected. However, no deterioration of the VOC biodegradation capacity due to the change in the bacterial population was observed by the authors. This work clearly showed that microbial diversity could not be tightly controlled over long periods of time in open TPPBs. However, such variations in the microbial population structure do not necessarily imply deterioration of the biodegradation performance of the reactor as noted by Baptista et al. (2008). Consequently, more studies on the dynamics of microbial populations and their effect on macroscopic VOC biodegradation performance are required to obtain a more comprehensive understanding of the microbiology in TPPBs.

2.3. Reactor configuration

To date, TPPBs devoted to VOC biodegradation have been operated in several reactor configurations such as stirred tank reactors (STR), airlift (AL), biotrickling filters (BTF), biofilters (BF) and even bubble columns (BC) (Table 3). Despite the fact that the STR is the most common TPPB configuration, it is also the most energy-demanding system (Hernandez et al., 2011a; Littlejohns and Daugulis, 2009). Therefore, research on VOC biodegradation in TPPBs implemented in low energy-intensive reactors is an important practical issue for

full-scale applications. TPPBs were initially operated as two-stage systems coupling an abiotic VOC absorption step with VOC biodegradation in separated devices (Cesario et al., 1998; Yeom and Daugulis, 2001). Nevertheless, two-stage systems were rapidly replaced by one-step processes where absorption and biodegradation were performed in the same device. This change in the concept of TPPBs was likely prompted by the fact that biomass separation from the NAP after the biodegradation stage has been reported to be very difficult (Hernandez et al., 2012; Quijano et al., 2009a). Thus, NAP recycling when operating at high biomass concentrations may lead to clogging when the absorption device has a packing material, or foaming when the absorption device is not packed. On the other hand, NAP pumping represents additional energy requirements and results in more complex process control. In spite of this, some authors suggest that two-stage TPPBs can be highly effective systems for VOC biodegradation (Darracq et al., 2010b; Dumont et al., 2011). However, no experimental evidence regarding the superior performance of two-stage TPPBs over one-stage systems is, to the best of our knowledge, available in the literature.

TPPBs for VOC biodegradation have also been commonly implemented in BTFs, and this configuration has been shown to be stable for hydrophobic VOC biodegradation (Bailon et al., 2009; van

Table 3
Bioreactor configurations used for TPPB implementation.

Reactor configuration	NAP	Target VOC	Reference
Stirred tank	FC40	Toluene and oxygen	Cesario et al., 1997a
Stirred tank coupled to an absorption column	Hexadecane	Benzene	Yeom and Daugulis, 2001
Stirred tank	Silicone oil	Hexane	Muñoz et al., 2006
Stirred tank	Silicone oil	Hexane	Arriaga et al., 2006
Stirred tank	Styrene-butadiene copolymer, silicone rubber, Nylon 6,6,	Oxygen	Littlejohns and Daugulis, 2007
Stirred tank	Hexadecane	Benzene	Nielsen et al., 2006
Stirred tank	Hexadecane	Toluene	Boudreau and Daugulis, 2006
Stirred tank	Hexadecane	Oxygen	Clarke et al., 2006
Stirred tank	FC40, heptamethylnonane	α-pinene	Muñoz et al., 2008
Stirred tank	Solid styrene-butadiene copolymer	Toluene	Daugulis and Boudreau, 2008
Stirred tank	Silicone oil, heptamethylnonane, Elvax 360, Desmopan DP9370A, Kraton G1657	Oxygen	Quijano et al., 2009b Quijano et al., 2010a,c
Stirred tank	Silicone oil	Dichloromethane	Bailon et al., 2009
Stirred tank	Silicone oil	Methane	Rocha-Rios et al., 2009
Stirred tank	Silicone oil	Hexane	Hernandez et al., 2010
Stirred tank	Hytrel, Zytel, Engage, rubber tires, silicone rubber, Kraton	Methyl ethyl ketone, toluene, hexane	Hernandez et al., 2011b
Biotrickling filter	Silicone oil	Hexane	van Groenestijn and Lake, 1999
Biotrickling filter	Silicone oil	Styrene	Djeribi et al., 2005
Biotrickling filter	Silicone oil	dichloromethane	Bailon et al., 2009
Biotrickling filter	Silicone oil	Methane	Rocha-Rios et al., 2009
Biotrickling filter	Silicone oil	α-pinene	Montes et al., 2010
Biotrickling filter	Silicone oil	Hexane	Hernandez et al., 2011a
Biofilter	Silicone oil	Mainly hexane	Fazaelipoor and Shojaosadati, 2002
Biofilter	Silicone oil	Hexane	Arriaga et al., 2006
Airlift	Silicone oil, heptamethylnonane, Elvax 360, DesmopanDP9370A, Kraton G1657	Oxygen	Quijano et al., 2009b Quijano et al., 2010a,c
Airlift	Silicone oil and rubber beads	BTEX[*]	Littlejohns and Daugulis, 2009
Airlift	Silicone oil, heptamethylnonane, Elvax 880, Desmopan9370A, Kraton G1657	Methane	Rocha-Rios et al., 2011
Airlift	Silicone oil	Hexane	Hernandez et al., 2011a
Packed column coupled to a stirred tank	FC40	Ethene	Cesario et al., 1998
Packed column	Silicone oil	Dimethylsulphide,dimethyl-disulphide, toluene	Dumont et al., 2011
Bubble column	Silicone oil, decane, hexadecane, FC40	Oxygen	Dumont et al., 2006b
Bubble column	Silicone oil	Hexane	Hashemi et al., 2012

[*] Benzene, toluene, ethylbenzene and xylene.

Groenestijn and Lake, 1999). A recent comparative study showed that BTFs might support even a higher VOC mass transfer performance than STRs (Hernandez et al., 2011a). In this study, the amount of VOC transferred-to-P_G/V ratio was superior for the BTF configuration compared with the STR using silicone oil as a NAP in both configurations. The authors highlighted the fact that TPPBs implemented in STRs are often operated at very high P_G/V values, which is likely prohibitive from a scaling-up point of view (Quijano et al., 2010f). In this regard, some authors studied the biodegradation of air streams contaminated with BTEX and methane using TPPBs in ALR configuration (Littlejohns and Daugulis, 2009; Rocha-Rios et al., 2011). Although these authors concluded that VOC biodegradation was superior in their STR counterparts, the VOC biodegradation-to-P_G/V ratio was superior for the ALRs. Quijano et al. (2009b, 2010c) recorded lower O_2 mass transfer performance in an ALR compared with a STR under similar experimental conditions when using silicone oil, heptamethylnonane, Elvax or Kraton as NAPs. However, the ALR performed better than the STR when using Desmopan as a NAP, which highlights the relevance of the bioreactor-NAP pair selection.

The available literature supports a rough comparison among the most common bioreactor configurations for TPPB implementation in terms of power consumption. For instance, P_G/V values for TPPBs implemented in STRs often range from 0.2 to 15 kW $m_{reactor}^{-3}$ (Littlejohns and Daugulis, 2009; Quijano et al., 2010f; Rocha-Rios et al., 2010). However, it is important to stress that these P_G/V values only consider the energy required for the mechanical agitation and therefore, this value will be significantly increased if the power required for overcoming the liquid column height is considered (1 m water column equals 9.8 kPa of pressure drop). On the other hand, the P_G/V values reported for TPPBs implemented in ALRs range from 0.02 to 0.06 kW $m_{reactor}^{-3}$ (Hernandez et al., 2011a; Littlejohns and Daugulis, 2009). To the best of our knowledge, only Hernandez et al. (2011a) reported the power consumption of a TPPB implemented in a BTF configuration. These authors estimated a P_G/V value of 0.01 kW $m_{reactor}^{-3}$, which is in agreement with typical P_G/V values of 0.011–0.014 kW $m_{reactor}^{-3}$ reported for BTFs without NAP (data considering pressure drops of 0.2–0.25 kPa m^{-1} and including the power required for liquid recycling according to Estrada et al., 2011). Therefore, the development of innovative bioreactor configurations holding P_G/V values attractive for full-scale implementation (e.g. $P_G/V < 1$ kW $m_{reactor}^{-3}$, Quijano et al., 2010f) deserves further investigation.

TPPBs have also been operated in BF configurations but to a limited extent compared with STR, BTF or ALR systems. Despite the fact that there is empirical evidence regarding satisfactory VOC removal in TPPBs implemented in BFs (Arriaga et al., 2006; Fazaelipoor and Shojaosadati, 2002), a small fraction of the NAP was lost in the leachate. Moreover, the presence of a liquid NAP embedded in the packing material reduces its water holding capacity, particularly when organic packing materials are used (e.g. compost), likely leading to long-term instability problems due to low water availability. Finally, TPPBs have recently been implemented in a BC as a low energy-intensive system to treat hexane (Hashemi et al., 2012). These authors reached RE values of up to 76% using silicone oil as the NAP, which constitutes high biodegradation performance compared with other reactor configurations. However, further studies should be done to confirm such promising results. Therefore, the development of bioreactor configurations exhibiting a VOC biodegradation-to-operating cost ratio comparable with other traditional bioreactors (e.g. BF and BTF) is an important research area to be pursued.

3. Recent studies on gas treatment in TPPBs

3.1. Studies at steady loading conditions

Although some studies on the treatment of hydrophilic VOCs in TPPBs have been recently conducted, most research on TPPBs for off-gas treatment has focused on moderately hydrophilic and hydrophobic compounds. This might be due to the fact that conventional biological systems such as BTFs and BFs perform satisfactorily for the abatement of water soluble VOCs under steady state conditions (Revah and Morgan-Sagastume, 2005). Table 4 reviews the most recent and significant studies carried out for continuous VOC treatment in TPPBs according to the general VOC classification showed in Fig. 1.

Despite the extensive research effort in the field of TPPBs, there are only a few studies systematically evaluating the impact of the presence of a NAP during the treatment of moderately soluble compounds such as toluene, benzene or styrene. Unfortunately, in most cases the benefits of the addition of a NAP during steady state operation are rare. However, recent studies based on careful experimental designs have demonstrated the superior performance of TPPBs over traditional gas treatment systems for the removal of moderately water-soluble and hydrophobic VOCs. For instance, Bailon et al. (2009) systematically compared the performance of TPPBs implemented in STR and BTF configurations for the removal of dichloromethane. These authors reported that silicone addition resulted in a 25% improvement on the elimination capacity (EC) in the BTF, while a 160% improvement in EC was recorded in the STR relative to the control without the NAP. Alfa-pinene biodegradation enhancements by a factor of 5 and 10 in a TPPB operating as a STR were reported by Muñoz et al. (2008) using the perfluorocarbon FC40 and heptamethylnonane compared with the same reactor without the NAP, respectively. This VOC biodegradation enhancement was attributed to a high-performance gas/NAP/water mass transfer pathway, which was assumed to be the main transport mechanism when the NAP holds a high affinity for the VOC ($H_{G/NAP}$ of 0.000056 and 0.001370 for FC40 and heptamethylnonane, respectively). However, it is important to stress that both FC40 and heptamethylnonane are no longer recommended as NAPs due to their volatility (Section 2.1). Hernandez et al. (2012) operated a TPPB implemented in a STR with silicone oil and hydrophobic microorganisms at hexane loading rates of 64 g $m_{reactor}^{-3}$ h^{-1} and reported steady state ECs of 59 g $m_{reactor}^{-3}$ h^{-1}, which corresponded to EC improvements of 1500% over the control reactor without NAP. This important EC improvement was attributed to the high affinity of both hexane and the microorganisms towards the NAP, which allowed their growth immersed in silicone oil and therefore the use of the entire gas/NAP transfer pathway. On the other hand, Rocha-Rios et al. (2009) observed that the average methane EC in a TPPB implemented in a BTF with silicone oil increased up to 131% relative to a control without the NAP. The lower removal improvement for methane compared to the previous reported enhancement for hexane in TPPBs implemented with silicone oil was likely related to the lower affinity of silicone oil for methane (silicone oil has ~300 times more affinity for hexane than for methane). These studies therefore confirm that the potential of TPPBs for VOC biodegradation increases with the affinity of the NAP for the VOC. In spite of this, there are limits to the positive effects derived from a high affinity of the NAP toward the target VOCs. In some cases, too high affinity can lead to substrate sequestering problems, resulting in poor substrate release from the NAP and therefore in poor VOC removal when the biodegradation process occurs in the aqueous phase (Guieysse et al., 2001; Littlejohns and Daugulis, 2008).

3.2. Studies at transient loading conditions

Another advantage of TPPBs over conventional biofiltration systems is that TPPBs can perform better under transient loading conditions by overcoming both substrate toxicity and mass transfer limitations during such dynamic periods as shown by several authors (Bailon et al., 2009; Boudreau and Daugulis, 2006; Hernandez et al., 2011b; Nielsen et al., 2005). TPPBs provide an efficient technology to cope with sudden surges in VOC loading rates as shown in Table 5. For example, Boudreau and Daugulis (2006) were able to treat a toluene loading surge of 6000 g m^{-3} h^{-1} with REs greater than 94% in a TPPB operating as an STR with n-hexadecane as a

Table 4
Recent studies on TPPBs for the treatment of stable VOC loads.

NAP	NAP (%v/v)	Reactor configuration	Target VOC	Microorganism	Concentration (g m^{-3})	Load (g m^3 h^{-1})	Steady state EC (g m^3 h^{-1})	EC improvement relative to the control (%)	Reference
Hydrophilic and moderately hydrophilic VOCs									
Mixture of polymers(Hytrel 8206, Engage 8100, Engage 8842)	20	STR(a)	Methyl ethyl ketone	Bacterial consortium	0.5	29	29	0	Hernandez et al., 2011b
Silicone oil	10	STR(a)	Dichloromethane	*Hyphomicrobium* KDM2 and KDM4	8	450 (+)	325	160	Bailon et al., 2009
Silicone oil	10	BTF(a)	Dichloromethane	*Hyphomicrobium* KDM2 and KDM4	13.8	550 (+)	200	25	Bailon et al., 2009
Silicone oil	10	BTF(a)	Styrene	*Sporothrix variecibatus*	2.2	400 (+)	350	120	Rene et al., 2011
Mixture of polymers(Hytrel 8206, Engage 8100, Engage 8842)	20	STR(a)	Toluene	Bacterial consortium	0.5	29	22	0	Hernandez et al., 2011b
n-hexadecane	33	STR(a)	Toluene	*Achromobacter xylosoxidans* Y234	10	343	>323	0	Boudreau and Daugulis, 2006
Solid styrene butadiene (SB) polymer beads	16	STR(a)	Toluene	*Achromobacter xylosoxidans* Y234	10	343	>323	0	Boudreau and Daugulis, 2006
n-hexadecane	33	STR	Benzene	*Achromobacter xylosoxidans* Y234	5.6	142	141	(−)	Nielsen et al., 2006
Polymeric phase of silicone rubber pellets	10	STR	BTEX	BTEX degrading bacterial consortium enriched from petroleum contaminated soil	5.5	60	>57	(−)	Littlejohns and Daugulis, 2008
Silicone oil	10	Airlift	BTEX	BTEX degrading bacterial consortium enriched from petroleum contaminated soil	0.8	20	19	0	Littlejohns and Daugulis, 2009
Silicone rubber beads	10	Airlift	BTEX	BTEX degrading bacterial consortium enriched from petroleum contaminated soil	0.8	20	19	0	Littlejohns and Daugulis, 2009
FC 40	10	STR (a)	α-pinene	*Pseudomonas fluorescens* NCIMB 11671	0.4	24	10 (*)	525	Muñoz et al., 2008
Heptamethylnonane	10	STR (a)	α-pinene	*Pseudomonas fluorescens* NCIMB 11671	0.4	24	19(*)	1087	Muñoz et al., 2008
Silicone oil	5	STR(a)	α-pinene	Bacterial co-culture containing *Rhodococcus erythropolis* DCL14 and an unidentified bacterium	10	600 (+)	395	58	Montes et al., 2011b
Silicone oil	5	BTF (a)	α-pinene	Microbial consortium enriched from the leachate of a previously operated biofilter containing predominantly the fungus *Ophiostoma stenoceras,*	7.7	464(+)	464	100	Montes et al., 2010
Hydrophobic VOCs									
Silicone oil	10	STR	Methane	Methanotrophic consortium obtained from activated sludge	15.9	187	106	41	Rocha-Rios et al., 2009
Silicone oil	10	BTF	Methane	Methanotrophic consortium obtained from activated sludge	11.1	131	51	131	Rocha-Rios et al., 2009
Silicone oil	5	STR	Methane	Methanotrophic consortium obtained from activated sludge	5.5	65	41	24	Rocha-Rios et al., 2010
Silicone oil	10	STR	Methane	Methanotrophic consortium obtained from activated sludge	5.5	65	48	45	Rocha-Rios et al., 2010
Silicone oil	10	Airlift	Methane	Methanotrophic consortium enriched from activated sludge	20	171	17	0	Rocha-Rios et al., 2011
Desmopan 9370A	10	Airlift	Methane	Methanotrophic consortium enriched from an activated sludge	20	171	17	0	Rocha-Rios et al., 2011
Silicone oil	10	STR (a)	Hexane	*Fusarium solani* (CBS 117476)	3	180	120 (*)	140	Arriaga et al., 2006
Silicone oil	5	BF	Hexane	*Fusarium solani* (CBS 117476	3	180	165 (*)	50	Arriaga et al., 2006
Hydrophobic VOCs									
Silicone oil	10	STR (a)	Hexane	*Pseudomonas aeruginosa*	3	180	135 160(*)	350 255	Muñoz et al., 2006
Silicone oil	20	STR (a)	Hexane	*Pseudomonas aeruginosa*	2.1	66	11 19 (*)	80 228	Hernandez et al., 2010
Kraton G1657	20	STR(a)	Hexane	*Pseudomonas aeruginosa*	2.1	66	6	0	Hernandez et al., 2010

Table 4 (continued)

NAP	NAP (%v/v)	Reactor configuration	Target VOC	Microorganism	Concentration (g m^{-3})	Load (g m^3 h^{-1})	Steady state EC (g m^3 h^{-1})	EC improvement relative to the control (%)	Reference
Silicone oil	20	STR(a)	Hexane	Hydrophobic hexane degrading bacterial consortium	2.1	64	60	1500	Hernandez et al., 2012
Silicone oil	10	STR (a)	Hexane	Hydrophobic hexane degrading bacterial consortium	0.5	24	21	1800	Muñoz et al., in press
Mixture of polymers (Hytrel 8206, Engage 8100, Engage 8842)	20	STR (a)	Hexane	Bacterial consortium	0.5	29	2	0	Hernandez et al., 2011b
Silicone oil	33 (#)	BF	Hexane	n-hexane degrading bacteria (dominant bacterium *Pseudomonas stutzeri*)	7	Data not shown	167 (*)	45	Fazaelipoor et al., 2006
Silicone oil	9	Bubble column	Hexane	Hexane degrading cell cultures enriched from an activated sludge	1.6	33	9	65	Hashemi et al., 2012
Silicone oil	9	Bubble column (a)	Hexane	Hexane degrading cell cultures enriched from an activated sludge	1.6	33	25	105	Hashemi et al., 2012

(a) Periodic aqueous culture broth refreshment.
(*) Maximum EC values.
(−) Control experiments were not carried out.
(+) Experiments at higher loading rates were carried out in the presence of a NAP.
(#) NAP weight/packing material weight (% w/w).

NAP, compared to REs of 45 % in a similar system without a NAP. Despite several studies showing no VOC biodegradation enhancements under steady state conditions in the presence of solid polymers, most studies of transient loadings have reported performance enhancements during TPPB operation (Boudreau and Daugulis, 2006; Hernandez et al., 2011b; Littlejohns and Daugulis, 2008). Therefore, NAP addition (e.g. such as an inexpensive solid polymer) can provide a "background" protection from shocks during transient loadings to any biofiltration system, which would enhance process stability and robustness, with minimal additional cost.

3.3. TPPB performance under more realistic scenarios

TPPB technology is particularly well suited for overcoming both VOC mass transfer limitations as well as toxicity problems during transient loading conditions (Muñoz et al., 2007). Nevertheless, mass transfer limitations are expected when treating hydrophobic VOCs (H > 1), while toxicity problems due to sudden VOC surges are more likely to occur when treating hydrophilic and moderately hydrophilic VOCs (H < 1). Thus, in real scenarios where mixtures of hydrophobic and hydrophilic VOCs are present in the waste gas stream, mass transfer limitations and toxicity problems can arise simultaneously. At this point, it is worth noting that most studies on VOC biodegradation in TPPBs have been undertaken with a model VOC or with mixtures of very similar pollutants (e.g. BTEX). To the best of our knowledge, the only study including a mixture of VOCs with very different hydrophobicities (methyl ethyl ketone, toluene and hexane) was reported by Hernandez et al. (2011b). In this work the TPPB did not perform better than the control without NAP during steady state operation, with the biodegradation performance decreasing with increased VOC hydrophobicity. However, under transient loading conditions the TPPB did perform better than the control, avoiding drastic drops in methyl ethyl ketone and toluene removal. Therefore, more studies utilizing VOC mixtures with different hydrophobicities are necessary to assess the potential of TPPBs under more realistic scenarios. In this regard, some related aspects could be considered. For instance, if the biomass is located in the aqueous phase, a NAP with high affinity for hydrophilic VOCs should be chosen to buffer potential substrate surges. However, the removal of hydrophobic VOCs in this case would be low due to the preferential affinity of the selected NAP for the hydrophilic VOCs. In contrast, if the biomass is located inside a liquid NAP, such a NAP must possess a high affinity for hydrophobic VOCs. In this way, surges of hydrophilic VOCs would not damage the biocatalytic activity due to the low affinity of the selected NAP for hydrophilic VOCs. Moreover, the removal of hydrophobic VOCs would remain high since biomass would be sufficiently concentrated in the NAP to resist periods of high hydrophobic VOC loadings.

Another option to cope with VOC mixtures is NAP tailoring in order to design non-aqueous phases with affinity for both hydrophilic and hydrophobic VOCs (Amsden et al., 2003; Littlejohns and Daugulis, 2008). In this context, a tailored NAP may consist of a mixture of NAPs with different hydrophobicities, solid polymers being likely more suitable for this kind of tailoring than liquid solvents due to practical aspects such as facilitated storage, handling of spills, safety, and recovery and reuse of the NAP (Daugulis et al., 2011). However, no studies reporting an enhanced biodegradation of VOC mixtures under both steady state and transient loading using tailored NAPs have been reported.

3.4. Influence of the operating conditions

While some experimental data are available in the literature evaluating the performance of TPPBs operated in STR mode under transient loadings (Boudreau and Daugulis, 2006), few data are available for BTFs. The first work on this topic was conducted by Bailon et al. (2009) who observed that the two-phase STR was less inhibited during dichloromethane surges (13-fold increase loading) than the two-phase BTF. While the two-phase STR showed an improvement in elimination capacity of 36 % compared with the control, the two-phase BTF did not show any improvement with respect to the control. These response differences might be explained by the gas flow regime in each of these systems: the STR is a completely mixed reactor while the BTF presents a plug-flow regime. In the STR, the high inlet concentration was immediately diluted within the whole reactor volume and thus, the microorganisms were actually not exposed to very high substrate concentrations during the surge load. However, in the BTF, the attached biomass was directly exposed to the high inlet concentrations.

Studies performed in several reactor configurations concluded that the removal of inhibitory accumulated metabolites is a key issue affecting stable long-term operation of conventional gas treatment biotechnologies

Table 5
Recent studies on TPPBs for the treatment of transient VOC loads.

NAP	NAP (%v/v)	Reactor configuration	Target VOC	Initial Load (g m^3 h^{-1})	X-fold increase loading	Duration of the step increase (h)	Transient overall EC (g m^3 h^{-1})	EC improvement relative to the control** (%)	Reference
Hydrophilic and moderately hydrophilic VOCs									
Mixture of polymers (Hytrel 8206, Engage 8100, Engage 8842)	20	STR	Methyl ethyl ketone	29.3	2	4	29.3	16	Hernandez et al., 2011b
Mixture of polymers (Hytrel 8206, Engage 8100, Engage 8842)	20	STR	Toluene	29.3	2	4	22.3	0	Hernandez et al., 2011b
Silicone oil	5	STR	α-pinene	80	12.5	8	500 (*)	150	Montes et al., 2011a
n-hexadecane	33	STR	Toluene	343	7 17	1 1	2328(*) 5640(*)	87 108	Boudreau and Daugulis, 2006
Solid styrene butadiene (SB) polymer beads	16	STR	Toluene	343	7 17	1 1	2138(*) 3600(*)	73 33	Boudreau and Daugulis, 2006
Silicone oil	10	STR	Dichloromethane	15	13.3	6	190(*)	36	Bailon et al., 2009
Silicone oil	10	BTF	Dichloromethane	15	13.3	6	120(*)	0	Bailon et al., 2009
Polymeric phase of silicone rubber pellets	10	STR	BTEX	60	2 4 6	4 4 4	134 282 230	(−) (−) (−)	Littlejohns and Daugulis, 2008
Silicone oil	10	Airlift	BTEX	20	3	4	37.2	40	Littlejohns and Daugulis, 2009
Silicone rubber beads	10	Airlift	BTEX	20	3	4	38.6	43	Littlejohns and Daugulis, 2009
n-hexadecane	33	STR	Benzene	62	10	4	620	(−)	Nielsen et al., 2005
Hydrophobic VOCs									
Mixture of polymers (Hytrel 8206, Engage 8100, Engage 8842)	20	STR	Hexane	29.3	2	4	0.6 (*)	0	Hernandez et al., 2011b

(*) Minimum EC of the step.
(−) Control experiments were not carried out.
** Control refers to the same reactor deprived of a NAP.

and TPPBs for off-gas treatment of hydrophobic VOCs (Hernandez et al., 2012; Muñoz et al., in press; van Groenestijn and Lake, 1999). The first systematic long-term study showing stable hexane biodegradation in a TPPB was performed by van Groenestijn and Lake (1999) who highlighted the relevance of a periodic refreshment of the aqueous phase to maintain stable high-performance operation. The relevance of this aqueous broth exchange was likely related to the removal of inhibitory metabolites causing unstable biodegradation performance. The key role of aqueous culture medium replacement was also recently shown by Hashemi et al. (2012). These authors reported hexane ECs 65% higher than those reported in the control system in a BC operating with silicone oil, while EC enhancements of 105 % were achieved when the aqueous culture broth of the TPPB was replaced daily by fresh mineral salt medium at a dilution rate of 0.034 day^{-1}. Consistent with these findings, Nielsen et al. (2006) found that if potentially detrimental metabolic intermediates do not accumulate in the medium, cellular viability and therefore the performance/stability of the process can be maintained over long periods in a closed liquid system without the need of medium exchange. In this regard, high ECs have been reported in a TPPB under discontinuous VOC loadings (e.g. VOC loadings applied for 10 h day^{-1}), while under continuous VOC loading the performance of the TPPB gradually declined (Aldric and Thonart, 2008). These results suggest that under discontinuous gas feeding, any potential inhibitory metabolite is degraded during the VOC starvation periods, while under continuous loading these metabolites likely accumulate, with the subsequent deterioration in the EC of the process. To the best of our knowledge, only Muñoz et al. (in press) performed a metabolite characterization of the cultivation broth of a TPPB treating air contaminated with hexane. Hexanol was the only detected metabolite from the aerobic hexane biodegradation pathway. However, the authors stressed that the metabolite-NAP interactions severely hindered the

quantification of these metabolites. Therefore, further studies including the monitoring of metabolite accumulation must be done to clearly demonstrate the role of aqueous medium refreshment.

The effect of surfactant addition on the performance of TPPBs has been recently assessed. Galindo et al. (2011) observed that the increased solubility and bioavailability of hexane and toluene arising from the addition of polyoxyethylene-polyoxypropylene block copolymer (surfactant commercially referred as Pluronic F-68) in the presence of silicone oil was not correlated to enhancements in their biodegradation. In contrast, Aldric et al. (2009) showed that the surfactant extract produced by *Rhodococcus erythropolis* increased the overall interfacial area for mass transfer, increasing the volumetric mass transfer coefficient. However, the authors also observed that when the biomass concentration exceeded 1 g L^{-1} the interfacial area was significantly hindered. The authors concluded that the interaction between microorganisms-NAP must be carefully considered in TPPB design since it can play an important role in the mass transfer phenomena and consequently on VOC biodegradation performance.

4. Modeling of TPPBs

TPPBs are complex multiphase systems that represent a challenge from a mathematical modeling point of view. The occurrence of simultaneous transfer pathways for both VOCs and O$_2$ makes experimental determination of the individual mass transfer coefficients involved very difficult. In this context, the direction of the mass transfer pathways will be determined by the phase in which VOC biodegradation occurs (water or NAP). So far, two main modeling approaches have been proposed to characterize the mass transfer in TPPBs depending on whether the aqueous phase and the NAP are considered as a single

phase, or as separate phases, the latter considering partial mass transfer pathways (Fig. 2).

In the first modeling approach the total VOC (or O_2) mass transfer rate from the gas to the water/NAP phase ($F_{G/mix}$) is described by the following general model:

$$F_{G/mix} = \bar{K}_L a(C_{mix}^* - C_{mix}) \tag{1}$$

where $\bar{K}_L a$ is the overall volumetric mass transfer coefficient from the gas to the water/NAP phase, while C_{mix}^* and C_{mix} are the saturation and the actual VOC (or O_2) concentration in the water/NAP mixture, respectively. The saturation concentration in the water/NAP phase is given by:

$$C_{mix}^* = \varphi_W \frac{C_G}{H_{G/W}} + \varphi_{NAP} \frac{C_G}{H_{G/NAP}} \tag{2}$$

where ϕ_W and ϕ_{NAP} are the volume fractions of water and NAP, respectively; while $H_{G/W}$ and $H_{G/NAP}$ are the dimensionless gas/water and gas/NAP partition coefficients for the VOC/O_2, respectively. The model arising from Eqs. (1) and (2) was initially proposed by Ho et al. (1990) and is the most common strategy to characterize the mass transfer performance in TPPBs (Quijano et al., 2009a). However, this simple model, despite giving insights into the mass transfer characteristics, is not useful when trying to perform comparisons among several TPPBs, as has been noted in the literature review of Clarke and Correia (2008). These authors identified three different behaviours of $\bar{K}_L a$ depending on the type and fraction of the NAP: (i) $\bar{K}_L a$ initially increases with NAP addition and subsequently decreases when the fraction of NAP increases over a critical value (ii) $\bar{K}_L a$ increases steadily at increasing NAP fractions without a subsequent decline and (iii) the addition of a NAP does not modify the $\bar{K}_L a$. However, the three behaviours have been reported to occur with the same NAP and under similar experimental conditions (e.g. n-hexadecane), which clearly indicates that the effect of NAP addition on mass transfer performance cannot be adequately characterized by means of $\bar{K}_L a$ alone. In this regard, Quijano et al. (2010e) reported that below a threshold power input value of ~600 W m^{-3}, $\bar{K}_L a$ measurements are subject to large experimental errors. They concluded that such errors might be related to failures in the fundamental assumption regarding the water/NAP phase homogeneity required to determine $\bar{K}_L a$. Recently, Littlejohns et al. (2010) proposed that the overall mass transfer coefficient ($\bar{K}_L$) can be obtained considering both aqueous and NAP resistances to mass transfer according to:

$$\frac{1}{\bar{K}_L} = \frac{1}{k_{NAP} \times H_{W/NAP}} + \frac{1}{k_W} \tag{3}$$

where k_{NAP} and k_W are the individual mass transfer coefficients on the NAP and aqueous phase side, respectively; while $H_{W/NAP}$ is the VOC/O_2 partition coefficient between water and the NAP. Nevertheless, k_{NAP} and k_W require an estimation from semi-empirical equations, and the error associated with these estimations is sometimes unknown. Moreover, the overall interfacial area for mass transfer must also be estimated or measured, which may increase the uncertainty associated with $\bar{K}_L$. Therefore, the use of overall mass transfer coefficients to describe the complex mass transfer phenomena of TPPBs may have limited utility.

Few studies have been devoted to quantifying the partial mass transfer pathways in TPPBs. The occurrence of several and simultaneous mass transfer pathways has challenged the experimental description and quantification of such partial transfer processes. As shown in Fig. 2, a general mass transfer model describing the total VOC/O_2 transferred from the gas to the NAP and aqueous phase (F_{TOT}, g m^{-3} h^{-1}) can be written as follows:

$$F_{TOT} = F_{G/W} + F_{G/NAP} \tag{4}$$

It is important to highlight that VOC and O_2 uptake may occur in both the water and the NAP phases as recently reported (Hernandez et al., 2012; Muñoz et al., in press). Hence, at steady state the following considerations must be taken into account: (i) if VOC/O_2 uptake occurs in the NAP, $F_{G/W} = F_{W/NAP}$ and (ii) if VOC/O_2 uptake occurs in the aqueous phase, $F_{G/NAP} = F_{NAP/W}$. Thus, $F_{G/W}$ can be written as follows:

$$F_{G/W} = k_L^{G/W} a\left(\frac{C_G}{H_{G/W}} - C_W\right) \tag{5}$$

where $k_L^{G/W} a$ is the partial volumetric mass transfer coefficient between the gas and aqueous phases. Likewise, $F_{G/NAP}$ can be expressed as:

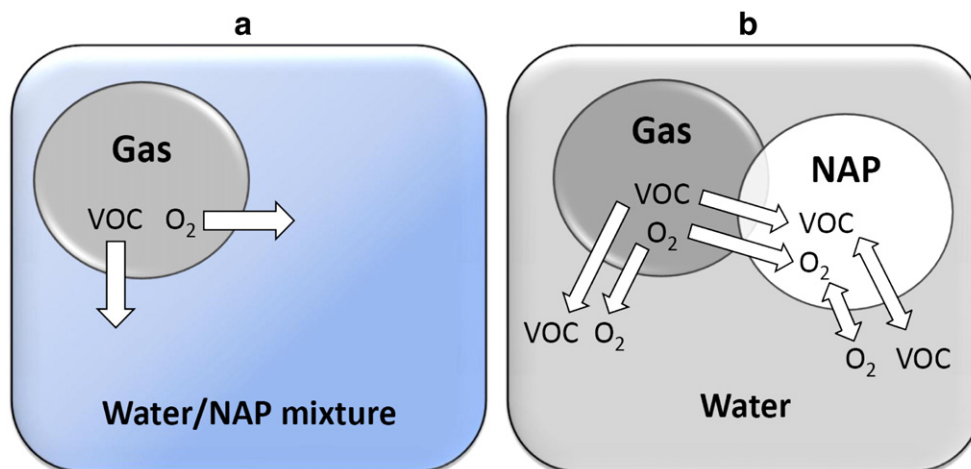$$F_{G/NAP} = k_L^{G/NAP} a\left(\frac{C_G}{H_{G/NAP}} - C_{NAP}\right) \tag{6}$$

Fig. 2. Mass transfer models considering that (a) the NAP and the aqueous phase constitute a homogeneous liquid phase and (b) considering the partial mass transfer rates between the aqueous phase and the NAP.

where $k_L^{G/NAP}a$ is the partial volumetric mass transfer coefficient between the gas phase and the NAP. From Eqs. (5) and (6), it is clear that in order to perform a complete mass transfer characterization the determination of $k_L^{G/W}a$, $k_L^{G/NAP}a$, C_W and C_{NAP} under the same experimental conditions for both VOC and O_2 is required. Moreover, the determination of $F_{G/W}$ in the absence of a NAP does not correspond to $F_{G/W}$ in a TPPB since the presence of a NAP strongly modifies $k_L^{G/W}a$ as demonstrated by Quijano et al. (2009b, 2010a). Cesario et al. (1997b) performed a comprehensive study on modeling and mass transfer characterization of TPPBs using a mass transfer enhancement factor based on Eqs. (4)–(6). Although the mathematical model was consistent, a poor fit between the model and experimental data was obtained. The authors attributed this lack of fit to the fact that partial mass transfer coefficients were estimated from available correlations (developed for single liquid phase systems) rather than being experimentally determined. Moreover, their modeling framework considered that the NAP addition did not affect the overall interfacial area for mass transfer; this assumption may be another source of error since NAP addition indeed induces strong modifications of the interfacial areas for mass transfer (Galindo et al., 2000; Quijano et al., 2010a). Therefore, the use of empirical correlations to estimate $k_L^{G/W}a$ or $k_L^{G/NAP}a$ must be carefully considered to avoid large errors in mass transfer characterization. Nielsen et al. (2007a,b) developed a model to describe the benzene vapor transfer and biodegradation in a TPPB using partial mass transfer coefficients. These authors estimated the mass transfer coefficients by least-square regression from empirical data, and they theoretically inferred the occurrence of a VOC/O_2 uptake in the NAP. Although many studies previously suggested such uptake in the NAP (or at the NAP/water interface), this is the only report where this information was inferred from a mathematical model. The work of Nielsen et al. (2007a) also included a sensitivity analysis, which predicted the relevance of microbiology on the performance of the TPPBs. The analysis indicated that enhanced substrate uptake in TPPBs can be attained with microorganisms whose kinetic parameters μ_{max} and K_s are maximized and minimized, respectively. This theoretical information is also in agreement with the modeling work on TPPBs of Littlejohns et al. (2010).

Fazaelipoor (2007) developed a mathematical model to evaluate VOC mass transfer and biodegradation in a TPPB under steady state conditions. This study, despite being purely theoretical, predicted that NAP addition is beneficial only when the microorganisms have a high affinity for the target VOC (small half-saturation constant) and the VOC is not toxic to the microorganisms (large VOC inhibition constant). Unfortunately, the half-saturation constant for the VOC in this work was normalized using the VOC concentration in the gas phase, which besides making this parameter dimensionally inconsistent, overestimates the effect of the parameter on the biodegradation performance. A different experimental and modeling approach was proposed by Quijano et al. (2009b) to characterize both $F_{G/W}$ and $F_{G/NAP}$ using O_2 as a model hydrophobic compound and a modified sulfite method to create an artificial O_2 uptake in the aqueous phase. Under these conditions C_W equaled zero due to the fast oxidation reaction between sulfite and O_2 in presence of a catalyst. Then, by measuring C_{NAP} and the sulfite oxidation rate, the maximum O_2 transfer rates for the gas/water and the gas/NAP pathways at steady state were obtained. This study revealed that the gas/water was the preferential transfer pathway for O_2 and that the presence of a NAP increased the gas/water transfer rate compared with the control without NAP.

Recently, mathematical models with lumped mass transfer coefficients have been developed to determine the maximum VOC/O_2 fraction transferable from the gas to the aqueous phase in TPPBs (Bordel et al., 2010; Hernandez et al., 2011a). This mass transfer characterization approach, despite not allowing individual quantification of $k_L^{G/W}a$ or $k_L^{G/NAP}a$, was used to compare the mass transfer performance of several reactor configurations. In this regard, the

work of Hernandez et al. (2011a) showed that TPPBs implemented in a BTF support a superior VOC mass transfer performance compared with STRs and ALRs.

In brief, despite important advances having been achieved in the last five years in the understanding of mass transfer mechanisms in TPPBs, mathematical modeling of these systems is still at an early stage. Thus, the observation of Dumont and Delmas (2003) regarding the lack of experimental data on partial mass transfer coefficients is still valid today. Hence, innovative experiments and theoretical studies are necessary to quantify the partial mass transfer coefficients. Some insights to reach this goal might arise from: (i) the study of TPPBs under mass transfer limiting conditions where both C_W and/or C_{NAP} would be negligible (as proposed by Quijano et al., 2009b) and (ii) the estimation of the partial VOC transfer coefficients from the coefficient measured for O_2 by means of diffusivity correlations as proposed by Littlejohns et al. (2010).

5. Conclusions and future challenges

TPPBs constitute an innovative technology for the treatment of hydrophobic and moderately soluble VOCs with proven superior performance and stability relative to their conventional biological counterparts. The full potential of TPPBs is achieved when operating with hydrophobic VOCs, whose biodegradation is intrinsically limited by mass transfer and where the new gas-NAP transfer pathway supports increased transfer rates. Foaming, adhesion to reactor internals and NAP emulsification have been identified as key constraints for TPPB implementation with liquid NAPs. However, while such constraints hold for TPPBs utilizing hydrophilic microorganisms, many of these drawbacks can be overcome by confining the biocatalytic activity within the NAP. Hence, the implementation of TPPBs with hydrophobic microorganisms opens both the possibility to further increase the biodegradation potential of TPPBs and new research opportunities. Solid NAPs have been shown to improve process robustness in the case of water soluble and sparingly soluble VOCs during transient operation, and have the potential to be tailored to VOC mixtures of varying hydrophobicities. Finally, the optimization of the power consumption is probably the main challenge that TPPB technology must overcome before being considered for full-scale applications. In this regard, research on new reactor configurations and operation strategies will certainly reduce the energy consumption per unit volume of treated air to those of well established biological systems such as BFs or BTFs and help to move TPPBs from an innovative to a mature technology.

Acknowledgments

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