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Two-phase partitioning bioreactors: towards a new generation of high-performance biological processes for VOC and CH_4 abatement.

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ABSTRACT The intense research and development conducted over the past 30 years in the field of air pollution control have increased the acceptance of biotechnologies as cost-efficient technological solutions to mitigate atmospheric pollution. Despite the low operating cost of biofilters and biotrickling filters, the limited mass transfer rates of certain key air contaminants from the gas phase to the microbial community and the perceived limited robustness of biotechnologies still make physical-chemical technologies the preferred methods for air pollution control. In this context, the addition of a non-aqueous phase to conventional bioreactors, in the so called two-phase partitioning bioreactors (TPPBs), can overcome the above mentioned limitations and trigger the consolidation of biotechnologies for the removal of odors, volatile organic contaminants (VOCs) or greenhouse gases. TPPBs have been successfully implemented in stirred tank, airlift, biofilter and biotrickling filter reactors for the removal of hydrophobic VOCs and CH_4 at unprecedentedly high removal rates. The high affinity of the non-aqueous phase for the target gas pollutant creates a new and efficient mass transfer pathway and increases process robustness compared to conventional biotechnologies. Finally, recent studies have shown that the use of hydrophobic biomass can boost the abatement performance of TPPBs by one order of magnitude.

KEYWORDS biphasic bioreactors, biological off-gas treatment, non-aqueous phase, mass-transfer enhancement, VOCs.

Introduction

The specialized Cancer Agency of the World Health Organization (WHO) classified outdoors air pollution as a human carcinogenic for lung and bladder cancer. Outdoor air pollution, which in 2010 was responsible for the death of 223.000 lung cancer patients, is mainly caused by transportation, stationary power generation, industrial and agricultural emissions, and residential heating and cooking [WHO, 2013]. In addition, gas pollutants such as CH_4 or chlorofluorocarbons are known to significantly contribute to global warming and stratospheric O_3 depletion, respectively, and are subjected to emission control programs worldwide [IPCC, 2013]. However, both atmospheric pollution legislations and their enforcement have not been traditionally as stringent as in wastewater or solid waste pollution management, likely due to the lack of strong evidences linking atmospheric pollution to chronic effects on human health or to the damage to natural ecosystems [De Nevers, 2003]. However, the minimization of emissions of volatile organic pollutants (VOCs) and CH_4 in this XXI century will be crucial to mitigate atmospheric pollution and will likely reach the deserved attention by governments and Environmental Agencies worldwide.

When modifications in the design and operation of the polluting industrial process are not sufficient to either reduce the levels of gas pollutants below legislation limits or mitigate the impact on the nearby population, the implementation of end-of-pipe treatment technologies is mandatory [Lebrero et al., 2011; Kennes and Thalasso, 1998]. Unlike wastewater treatment, where biological treatment technologies dominate the market worldwide, a totally different scenario is found nowadays when selecting VOCs and odor treatment technologies [Estrada et al., 2012a]. In this regard, when public concern about atmospheric pollution arised in the early 1960s, physical chemical technologies such as activated carbon filtration, chemical scrubbing or incineration were already mature technologies, while biotechnologies for off-gas treatment were still at an incipient stage. Forty years later, biotechnologies have become a mature technology capable of providing consistent treatment efficiencies and meanwhile the prices of energy and chemicals have rapidly increased. These two facts have promoted the implementation of biological off-gas treatment technologies worldwide. Biological gas treatment processes are based on the catalytic action of microorganisms to oxidize the gas pollutants to CO_2, water, biomass, sulphate etc. [Revah and Morgan-Sagastume, 2005]. A recent sustainability study conducted by Muñoz and co-workers clearly showed that despite exhibiting significantly higher investment costs, biotechnologies such as biofilters, biotrickling filters or activated sludge processes often present lower operating costs than their physical/chemical counterparts, which render them the most cost-effective option in the long-term operation [Estrada et al., 2011]. In addition, biotechnologies also present significantly lower environmental impacts since they operate at ambient pressure and temperature, yield CO_2, H_2O and biomass as non-hazardous end-products, and do not require the continuous addition of costly and hazardous reagents [Iranpur et al., 2005, Yang et al., 2010].

However, despite the above mentioned advantages, biological treatment methods are often limited by the low mass transfer of poorly water-soluble pollutants (e.g. hexane, CH_4, pinene) from the gas phase to the aqueous phase containing the microorganisms responsible of pollutant biodegradation [Arriaga et al., 2006; Muñoz et al., 2007; Muñoz et al., 2012]. This is especially true for biofilters including rotating drum biofilters and tubular biofilters, which are more suitable for the treatment of hydrophilic VOCs [Chen et al., 2012, Yang et al., 2008]. This limitation entails higher bioreactor volumes and therefore higher investment costs. Another process limitation in conventional biotechnologies arises from microbial inhibition or O_2 limitation during the treatment of high concentrations of water soluble or moderately soluble VOCs, especially during episodes of load surges [Daugulis and Boudreau, 2008, Nielsen et al., 2005]. The addition of an organic phase to the biological process, in the so called two-phase partitioning bioreactors (TPPBs), has the potential to overcome both limitations as a result of the high affinity of the organic phase for the target VOCs and O_2 [Cesario et al., 1997; Daugulis, 2001]. Likewise, the addition of surfactants can increase the aqueous solubility of hydrophobic VOCs and improve their abatement [Song et al., 2012, Yang et al., 2010, Wang et al., 2013].

Based on the intense research conducted in the field of TPPBs over the past 10 years, this review identifies and discusses the fundamentals of TPPBs, and their potential and limitations for overcoming some of the typical operational limitations encountered in conventional biological off-gas treatment systems. Recommendations are made for design and operation of TPPBs, while the challenges faced by this novel technology will be also highlighted and discussed to foster scaling up of this technology from the lab to full-scale applications.

Fundamentals

TPPBs, also known as biphasic systems, originated in the 1980s to increase both O_2 mass transfer in conventional fermentations and the yield of inhibitory byproducts such as ethanol or citric acid in the so-called extractive fermentation [Bruining et al., 1986; Rols et al., 1990; Malinowski, 2001]. This innovative operational approach was later applied in the Netherlands to the off-gas treatment of hydrophobic VOCs in bioscrubbers in 1992 [Poppe and Schippert, 1992; Cesario et al., 1997]. Two-phase partitioning bioreactors are characterized by the addition of a non-miscible, biocompatible and non-volatile organic phase with a high affinity for the target pollutants and O_2 [Daugulis, 2001; Quijano et al., 2009]. This higher affinity of the organic phase, also named non-aqueous phase (NAP), compared to water mediates a higher driving force for pollutant/O_2 mass transport from the gas to the liquid phase as a result of the increased pollutant/O_2 concentration gradients (Fig. 1) [Clarke and Correa, 2008]. The presence of a NAP in some particular bioreactor configurations (i.e stirred tanks) also mediates an increase in the gas-liquid interfacial area as a result of a decrease in the overall liquid surface tension, which can ultimately increase the mass transport of VOCs and O_2 to the microorganisms [Quijano et al., 2010a]. In addition, this high affinity entails a high solubility of the target pollutant (or its biodegradation metabolites) in the NAP, which provides the NAP with a unique capacity to buffer the process against sudden surges in VOCs loads and therefore in a superior process robustness [Lebrero et al., 2013; Hernandez et al., 2011a]. At this point it should be stressed that biotechnologies are still perceived by industry as a non-robust platform for off-gas treatment because they are emergent and often not properly operated and understood by plant managers and operators. However, a systematic robustness analysis recently conducted by the authors in collaboration with CH2MHill showed that classical biotechnologies are indeed robust [Estrada et al., 2012].

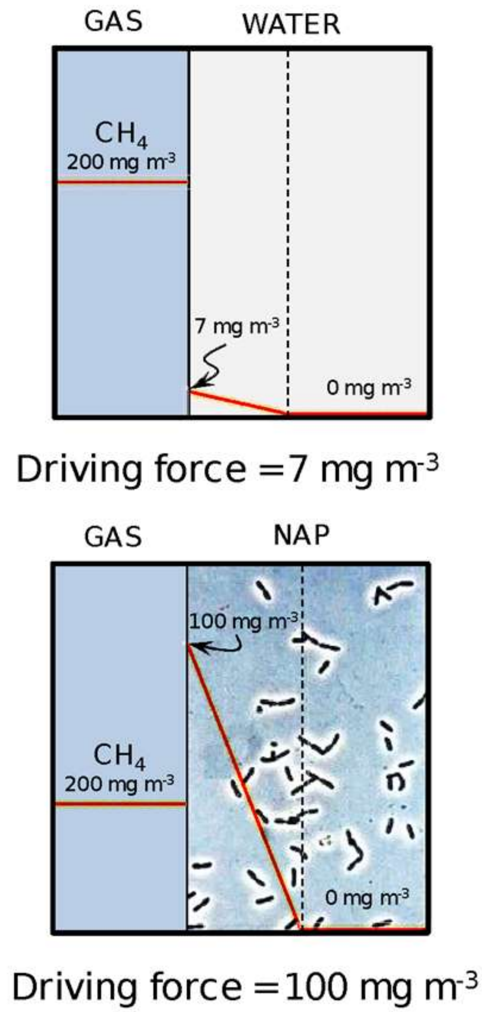

Figure 1 Gas-liquid mass transfer representation using the two-film theory for a diluted emission of CH_4 in (a) a conventional bioreactor and (b) a two-phase partitioning bioreactor provided with silicone oil.

The efficiency of TPPBs in the abatement of VOCs is determined by the target pollutant hydrophobicity, the properties of the organic phase, the characteristics of the microbial community and the bioreactor configuration selected [Muñoz et al., 2012]. The influence of these process variables on the VOC abatement performance of TPPBs are critically reviewed below.

Pollutant hydrophobicity vs. Pollutant Mass Transfer

Pollutant mass transfer from the gas phase to the aqueous phase containing the microbial community in conventional off-gas treatment bioreactors can be described as follows [Bordel et al., 2010]:

$$F_{G/W} = K_L^{G/W} a \left(\frac{C_G}{H_{G/W}} - C_W \right) \qquad \text{Eq. 1}$$

Where $F_{G/W}$ represents the volumetric pollutant mass transfer rate (g m^{-3} h^{-1}) from the gas to the aqueous phase, is the overall volumetric mass transfer coefficient (h^{-1}) between the gas and aqueous phase, C_G and C_W are the pollutant concentrations (g m^{-3}) in the gas and aqueous phase, respectively, and $H_{G/W}$ the dimensionless Henry's law constant (also named gas-water partitioning coefficient) for the target pollutant [Muñoz et al., 2007]. In this context, while is mainly determined by the configuration and operation of the bioreactor, the type of pollutant directly affects the concentration gradient available for mass transport (= driving force). Hence, water-soluble gas pollutants with $H_{G/W}$ of 0.0001-0.099 such as methanol, acetone, dimethyl sulfide do support high concentration gradients and their abatement would be hardly limited by mass transfer [Estrada et al., 2013]. On the other hand, gas pollutants such as CH_4, hexane, ethane, etc. are prone to undergo mass transfer limitations as a result of the low concentration gradients imposed by their high Henry´s law constant (in the range of 1 to 70). In the particular case of TPPBs, the gas-NAP partitioning coefficient of the pollutant is several orders of magnitude lower than its gas-water counterpart (Table 1), which significantly increases the concentration gradients available for pollutant mass transport [Kraakman et al., 2011].

Table 1 Gas-water and gas-NAP partitioning coefficients of typical gas pollutants for silicone oil.

Gas Pollutant	$H_{G/NAP}$	$H_{G/W}$	Reference
Methane	2.0	31	[Rocha-Rios et al., 2011] [Sanders, 1999]
Dimethyl sulfide	0.016	0.085	[Darracq et al., 2010] [Sanders, 1999]
Hexane	0.0058	74	[Hernandez et al., 2010] [Sanders, 1999]
Toluene	0.00064	0.25	[Darracq et al., 2010] [Sanders, 1999]
α-Pinene	0.00018	0.83	[Muñoz et al., 2008] [Sanders, 1999]

However, at this point it must be stressed that the expected enhancement in VOC biodegradation will not correspond to the exact ratio between $H_{G/NAP}$ and $H_{G/W}$ since the NAP in TPPBs is often present at percentages of 5-30 % and the NAP-water mass transfer pathway is not as efficient as the gas-NAP pathway [Muñoz et al., 2007]. In addition, the high pollutant mass transfer rates supported by the presence of a NAP might induce the release of inhibitory metabolites that might hinder the exploitation of the full potential of the gas-NAP mass transfer pathway [Hernandez et al., 2012].

Non-aqueous phase selection

The selection of the optimum NAP must be regarded as a holistic process, which involves the evaluation of the characteristics of VOCs to be biodegraded, the hydrodynamic behavior of the NAP in the bioreactor, its interaction with the microbial community, and several economic-environmental aspects that must be also considered from a sustainability point of view [Bruce and Daugulis, 2001; Muñoz et al., 2008; Quijano et al., 2010b]. In this regard, the affinity of the NAP for the target VOCs, quantified in terms of the gas-NAP partitioning coefficient, was initially consider the major selection criterion in TPPBs [Arriaga et al., 2006, Fazaelipoor, 2007]. This affinity determines both the pollutant mass transfer from the gas emission to the microbial community and the aqueous pollutant concentration during transient pollutant load surges [Hernandez et al., 2011a, Montes et al., 2011b]. However, both LittleJohns and Daugulis (2007) and Quijano et al. (2010b) observed that other NAP characteristics such the dispersion capacity of the NAP in the bioreactor or its gas bubble disruption potential, might also play a key role on the enhancement of gas pollutant transport. Desirable properties in a NAP are also its immiscibility in water (which minimizes NAP losses during purging or leaching and facilitate phase separation), non-volatility (in order to avoid NAP losses) and a different density than water (to facilitate phase separation). The interaction between the microbial community responsible for the biodegradation of gas pollutants and the NAP significantly impacts the performance of TPPBs. Thus, the ideal NAP selected must be non-toxic to the microbial community (as a rule of thumb organic solvents with a logarithm of the octanol-water partition coefficient higher than 4 are considered non-toxic), non-biodegradable (to avoid NAP losses and the preferential uptake of the NAP over the target gas pollutants). Furthermore, it would be highly desirable if it would support microbial growth inside the NAP to enhance microbial kinetics due to the higher VOCs and O_2 concentrations in the NAP [Ramos et al., 2002; Hernandez et al., 2012; Muñoz et al., 2012]. From an environmental viewpoint, NAPs must be non-hazardous and odorless, while a low cost and its availability in bulk quantities are desirable characteristics from a economic view point.

During the past 20 years of research in TPPBs devoted to off-gas treatment, the potential of both liquid and solid non-aqueous phases has been evaluated. Liquid non-aqueous phases such as ionic liquids often present toxicity issues and are significantly water soluble, while organic solvents such as hexadecane or diethyl-sebacate are readily biodegradable [Arriaga et al., 2006; Quijano et al., 2010c]. Likewise, the pioneering perfluorocarbons tested by Cesario and co-workers such as FC40 are potent O_3 depleting agents and highly volatile [Cesario et al. 1997; Cesario et al. 1998; Quijano et al. 2010b]. On the other hand, solid polymers such as katron™, Elvax™ or Desmopan™ did not support significant enhancements in the VOC degradation under steady state conditions despite exhibiting a significantly high affinity for these gas pollutants, but were capable of increasing process stability during operation at fluctuating VOCs loads [Hernandez et al., 2011a]. These operational and environmental constraints significantly reduce the number of NAPs suitable for implementation in TPPBs. As a matter of fact, silicone oil (polydimethylsiloxane) constitutes, to the best of our knowledge, one of the few solvents evaluated that satisfies all the above mentioned requirements [Dumont et al., 2011; Muñoz et al., 2007] and therefore it has been used in most off-gas treatment TPPBs studies. However, the presence of siloxanes in the treated gas from TPPBs operated with silicone oil must still be assessed. In this context, based on the proven potential of TPPBs for off-gas treatment applications, more research must be devoted to the formulation of synthetic organic solvents or polymers capable to cope with mixtures of VOCs of different hydrophobicity. As far as the authors know, only the group of Prof. A.J Daugulis has addressed this issue for the co-treatment of a mixture of hexane, toluene and methyl-ethyl-ketone tailoring a mixture of solid polymers [Hernandez et al., 2011a]. In addition, new organic solvents or polymer formulations are also needed to improve the mass transfer of scarcely-water soluble gas substrates such as CH_4 or O_2, which exhibit a very low solubility in silicone oil. In this context, the above discussed silicone oil-mediated enhancement in VOC abatement might be limited when treating high concentrations of hydrophobic VOCs as a result of limitations in oxygen mass transfer, since the O_2 concentration gradient available for mass transport between the gas phase and silicone oil might be one order of magnitude lower than those of hydrophobic VOCs.

Microbial activity in TPPBs determines both the catabolic spectrum of potentially biodegradable gas pollutants and the gas pollutant mass transfer rates [Revah and Morgan Sagastume, 2005; Muñoz et al., 2013]. To date, most studies on TPPBs devoted to gas treatment have been conducted under laboratory conditions using both pure and mixed microbial cultures [Muñoz et al., 2007; Bailon et al., 2009]. Mixed microbial culture experiments provide a more realist approach to TPPBs performance under real case scenarios, where sterile conditions are never maintained and the high microbial diversity confers the bioreactors with a higher resilience and robustness than pure culture [Briones and Raskin, 2003, Cabrol and Malhautier, 2011]. In this regard, pollutant concentration plays a key role on microbial diversity in TPPBs, with two-phase biotrickling filters treating VOCs at mg m^{-3} levels exhibiting very high microbial diversities compared to biotrickling filters operated at VOC concentrations in the range of g m^{-3} [Bailon et al., 2009; Estrada et al., 2012b, Lebrero et al., 2013]. No influence of the presence of the NAP on the microbial diversity was however found in the few studies addressing this issue at trace level concentration, ruling out the occurrence of a beneficial effect of the NAP on culture preservation [Lebrero et al., 2013]. Further studies at industrial level concentrations (˜g m^{-3}) must be conducted to confirm this phenomenon.

Traditionally, TPPBs operate with the microbial community confined in the aqueous phase (in direct contact with the nutrients required for microbial growth), where both pollutant and O_2 transport occur simultaneously via the gas/NAP/water pathway and gas/water pathway. In this particular scenario, the preferential VOC flux occurs via the gas/NAP/water pathway as a result of the high affinity of the NAP for the target VOC, despite the full potential of the gas/NAP pathway is limited by the NAP/water VOC mass transfer (the high affinity of the NAP for the VOC might result in low NAP/water transfer). The selection of this hydrophilic biomass is only based on its ability to mineralize the organic pollutants [Hernandez et al., 2012] (Fig 2a). Hence, VOC removal enhancement factors of 2 have been recorded during hexane biodegradation in stirred tanks supplemented with 20 % silicone oil compared to conventional aqueous-based systems. On the other hand, when microbial activity is confined in the organic phase, the full potential of the gas-NAP mass transfer pathway is exploited (Fig 2b).

Operation under this particular condition requires the isolation and maintenance in the TPPBs of a hydrophobic microbial community capable of growing immersed in the NAP, with nutrients slowing diffusing from the aqueous phase to the NAP (which could eventually limit TPPB performance) [Muñoz et al., 2013]. Biokinetic isolation strategies based on the wash-out of the biomass growing in the aqueous phase have been successfully tested for the isolation of a CH_4 degrading hydrophobic biomass at the Dept. of Chemical Engineering and Environmental Technology of Valladolid University. Preliminary evidences of the ability of microorganisms to grow at the water/NAP interface were reported by Ascon-Cabrera and Lebeault (1993,1995) during the degradation of ethyl butyrate and chlorobenzenes in TPPBs, and further confirmed by McLeod and Daugulis (2005) during the biodegradation of Polycyclic Aromatic Hydrocarbons in a TPPB constructed with Bis(ethyl-hexyl) sebacate. A definitive evidence of the ability of microorganisms to grow exclusively inside NAPs was recently reported by Hernandez et al. (2012) during hexane biodegradation in a TPPB implemented in a stirred tank supplemented with 20 % of silicone oil, where enhancement factors of 8 (compared to a similar TPPB with the microbial activity confined in the aqueous phase) were recorded.

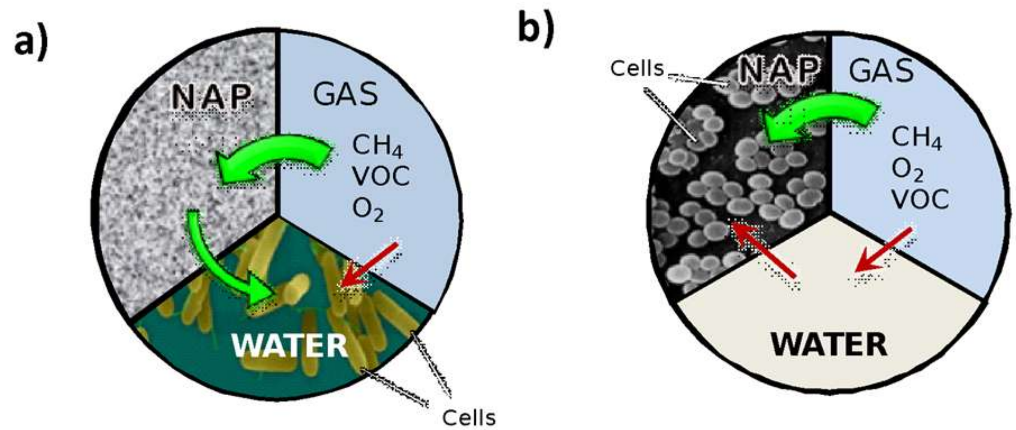

Figure 2 Gas pollutant and O_2 mass transfer pathways when the microbial activity is located in (a) the aqueous phase and (b) immersed in the non-aqueous phase. The thickness of the arrows is correlated with the mass flow rates.

More research is however needed in order to better understand the mechanisms underlying microbial growth and VOC and nutrient uptake in hydrophobic biomass-based TPPBs, based on the promising results so far obtained.

TPPB configurations

Two-phase partitioning bioreactors for air pollution control were originally implemented in two-stage configurations consisting of an absorption reactor containing the NAP and where the gas pollutants were adsorbed, coupled with a bioreactor devoted to their oxidation [Cesario et al., 1998; Yeom and Daugulis, 2000; Yeom et al., 2001]. However, the inherent technical difficulties to separate the NAP from the aqueous phase and biomass in the absorption reactor rapidly promoted the implementation of single-stage TPPBs where absorption and biodegradation simultaneously occur in the same unit. To date, TPPBs have been implemented in all existing off-gas treatment bioreactors: stirred tanks, biotrickling filters, biofilters, bubble columns, airlift and capillary reactors [Hashemi et al., 2012; Hernandez et al., 2012, Rocha-Rios et al., 2011; Van Groenestijn and Lake 1999; Rocha-Rios et al., 2013; Lebrero et al., 2014]. Stirred tank TPPBs offer a proficient control of NAP dispersion (proportional to the stirring rate) and environmental parameters such as pH, T, nutrient supply and metabolite removal from the cultivation broth. However, despite being the most commonly applied TPPB configuration in lab-scale studies to date, their high energy requirements (0.2-15 kW $m^{-3}_{reactor}$ without considering the energy for gas sparging) restrict the potential scale-up of this bioreactor configuration. The use of hydrophobic biomass, recently reported as a promising alternative capable of decreasing bioreactor volume needs by a factor of 17, has also challenged the use of stirred tanks as a platform technology for the implementation of TPPBs due to the technical difficulties associated to the dispersion of the biomass-NAP phase in the long-term operation (Fig. 3) [Muñoz et al., 2013].

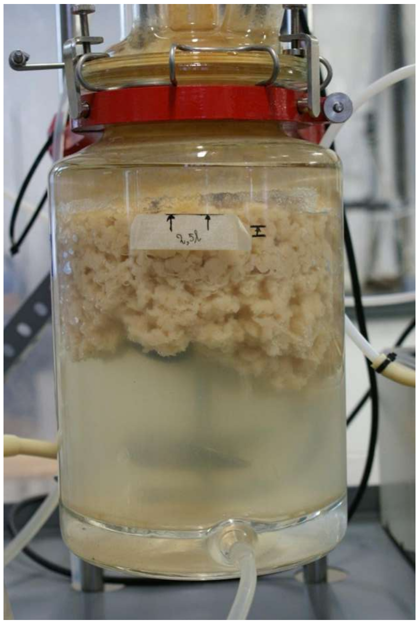

Figure 3 Appearance of the hydrophobic biomass during hexane biodegradation in a stirred tank reactor operated with 20 % of silicone oil.

Biotrickling filters, recently pointed out as the technology with lowest operation costs (yearly operating cost per m^3 h^{-1} of 1.2 €) among the most commonly used odor abatement technologies, were also pioneers as a platform for TPPBs to improve the mass transport of hydrophobic VOCs. Hence, Van Groenestijn and Lake (1999) reported a successful hexane removal in a biotrickling filter supplemented with silicone oil without significant silicone oil losses over a 6 months experimentation period. Dichloromethane removals 25 % higher than in a conventional biotrickling filter under similar operation conditions were also recorded in a BTF supplemented with silicone oil [Bailon et al., 2009]. Likewise, Hernandez et al. (2011b) recently assessed the mass transfer potential of three two-phase partitioning reactors (an airlift, a biotrickling filter and a stirred tank) using hexane as model VOC and silicone oil as a model NAP. This comparative study revealed both the superior mass transfer potential of two-phase partitioning biotrickling filters and their lower energy requirements (0.01 $kWm^{-3}{}_{reactor}$). In this regard, a two phase biotrickling filter treating a mixture of VOCs at trace level concentration (simulating an odorous emission) supported both a superior abatement performance for the most hydrophobic VOCs and an enhanced process robustness against sudden fluctuations in VOC loading compared to a conventional biotrickling filter [Lebrero et al., 2013]. Surprisingly, approximately 50 % of the NAP initially added to the biotrickling filter remained embedded in the packing material. Based on the performance data reported for stirred tank TPPBs operated with hydrophobic biomass, promising results are expected when using biotrickling filters with inorganic packing materials coated with silicone oil and hydrophobic biomass since the operation of this bioreactor configuration is not directly related to NAP dispersion.Conventional biofilters, constructed with both organic and inorganic supports, have been also successfully operated using silicone oil as mass transfer vector. For instance, Arriaga el al. (2006) achieved unprecedentedly high hexane elimination capacities (165 g m^{-3} h^{-1}) in a fungal perlite-based biofilter supplemented with 0.5 % of silicone oil, which represented a 50 % performance enhancement compared to NAP-deprived fungal biofilters. However, a significant NAP leaching from this inert support was recorded. In a recent study, Lebrero et al. (2014) evaluated the potential of a hexane-degrading hydrophobic biomass in a compost-based biofilter embedded with different ratios of silicone oil [Lebrero et al., 2014]. The two-phase partitioning biofilter supplemented with 10% of silicone oil exhibited 72% higher hexane elimination capacities than the control biofilter, without significant NAP leaching due to the good adhesion of silicone oil to compost. However, when 20% of silicone oil was added to the compost no removal enhancement was observed, likely due to a severe reduction in the water holding capacity of the packing media (which decreased by 71%) and to the occurrence of a silicone-oil mediated gas flow channelling. Due to their cost-effectiveness (0.06 kW $m^{-3}{}_{reactor}$), the potential of airlift bioreactors in combination with a NAP has been assessed for the abatement of CH_4 and BTEX [LittleJohns and Daugulis, 2009, Rocha-Rios et al., 2011]. Thus, the efficient BTEX removal performance reported by Littlejohns and Daugulis (2009) in an airlift system supplemented with silicone oil required process operation at low loading rates (20 g m^{-3} h^{-1}). In this particular bioreactor configuration, the dispersion of the NAP is directly determined by the gas flow rate treated (proportional to the inverse of the gas empty bed residence time), and a good

NAP dispersion would imply process operation at very low gas empty bed residence time, with the subsequent reduction in the abatement performance during the treatment of poorly or moderately soluble pollutants. An innovative airlift bioreactor with internal gas recirculation (which allowed decoupling NAP dispersion and the gas residence time) was successfully tested by Rocha-Rios et al. (2011) for the treatment of CH_4. In contrast to the airlift, Hashemi et al. (2012) obtained hexane removal efficiencies of 76 % using silicone oil as NAP in a bubble column TPPB. Finally, capillary reactors operating under Taylor flow, which can increase up two orders of magnitude the kla, and with silicone oil have shown to increase up to 47% the methane removal as compared to reactors without the NAP [Rocha-Rios et al., 2013].. In this context, despite enough information is nowadays available on the design and operation of lab-scale TPPBs configurations (Table 2), the implementation of this promising platform technology at pilot-scale is still needed to fully demonstrate the potential of TPPBs for off-gas treatment.

Table 2 Pollutant abatement performance of lab-scale TPPB configurations reported in the past 3 years.

Gas Pollutant	TPPB configuration	LR ($g\ m^{-3}\ h^{-1}$)	Concentration ($g\ m^{-3}$)	EC ($g\ m^{-3}$)	Reference
CH4	Stirred Tank with 10 % silicone oil	65	5.5	48	[Rocha-Rios et al., 2010]
CH4	Airlift with 10 % Desmopan™	171	20	17	[Rocha-Rios et al., 2011]
Hexane	Bubble column with 9 % silicone oil	33	1.6	25	[Hashemi et al., 2012]
Hexane	Stirred Tank with 20 % silicone oil	64	2.1	60	[Hernandez et al., 2012]
Hexane	Compost biofilter with 10 % silicone oil	30	0.6	23	[Lebrero et al., 2014]
Hexane	Stirred Tank with 10 % silicone oil	24	0.5	21	[Muñoz et al., 2013]
Hexane	Stirred Tank with 20 % kraton™	66	2.1	6	[Hernandez et al., 2010]
α-pinene	Biotrickling filter with 5 % silicone oil	464	7.7	464	[Montes et al., 2010]
α-pinene	Stirred Tank with 5 % silicone oil	600	10	395	[Montes et al., 2011]
Toluene	Stirred tank with 20 % of a mixture of Hytrel8206+Engage8100 + Engage8842	29	0.5	22	[Hernandez et al., 2011a]
Styrene	Biotrickling filter with 10 % silicone oil	400	2.2	350	[Rene et al., 2011]

Conclusions

Despite the potential of TPPBs increases when decreasing the gas-NAP partitioning coefficient, variables such as NAP hydrodynamics and the ability to host the microbial community inside have been recently included in the NAP selection criteria list. The fact that silicone oil constitutes the only non-aqueous phase fulfilling all operational, environmental and economic criteria highlights the need for new organic solvent or polymer formulations capable of improving the mass transfer of gas substrates with a poor-water solubility but low affinity for silicone oil. The use of hydrophobic biomass growing inside the NAP has been recently identified as the key to fully exploit the mass transfer potential of the NAP, and constitutes one of the most promising research area in the field of biological off-gas treatment. Biotrickling filters and biofilters exhibit a consistent VOC abatement performance with less operational problems and lower operating costs than stirred tanks, airlift or bubble columns bioreactors. The implementation of TPPBs in membrane bioreactors still remains as a promising niche for future research. Last but not least, pilot-scale tests are still necessary to move this technology forward from lab-scale to full scale.

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