



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.

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### 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

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## Nomenclature

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

### Greek symbols

$\phi$	Volume fraction (dimensionless)
$\mu_{\max}$	Maximum specific growth rate of the microorganisms ( $\text{h}^{-1}$ )

### 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  $5 \text{ g m}^{-3}$  (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  $\text{O}_2$  and consequently the  $\text{O}_2$  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  $\text{O}_2$  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  $\text{O}_2$  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

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