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## Removal of Hydrophobic Volatile Organic Compounds in an Integrated Process Coupling Absorption and Biodegradation – Selection of an Organic Liquid Phase

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1 **Removal of hydrophobic Volatile Organic Compounds**  
2 **in an integrated process coupling Absorption and**  
3 **Biodegradation – Selection of an organic liquid phase**

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22

## 23 Abstract

24 Since usual processes involve water as absorbent, they appear not always really efficient for the treatment of  
25 hydrophobic VOC. Recently, absorption and biodegradation coupling in a two-phase partitioning bioreactor (TPPB)  
26 proved to be a promising technology for hydrophobic compound treatment. The choice of the organic phase, the non-  
27 aqueous phase liquid (NAPL) is based on various parameters involved in both steps of the process, hydrophobic VOC  
28 absorption in a gas-liquid contactor, and biodegradation in the TPPB. VOC solubility and diffusivity in the selected  
29 NAPL, as well as NAPL viscosity, seems to be the main parameters during the absorption step, while biocompatibility,  
30 namely the absence of toxic effect of the NAPL towards microorganisms, non-biodegradability and VOC partition  
31 coefficient between NAPL and water were revealed as the key factors during the biodegradation step. The screening  
32 of the various NAPL available in the literature highlighted two families of compounds matching the required  
33 conditions for the proposed integrated process, silicone oils and ionic liquids.

34 **Key words:** *Hydrophobic VOC; Absorption; Two-phase partitioning bioreactor; Non-aqueous phase liquid;*  
35 *Silicone oils; Ionic liquids.*

36

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## 57 1. Introduction

58 With the matter of Global warming owing to the greenhouse effect, the treatment of atmospheric  
59 emission, including Volatile Organic Compounds, has become an ecological and economic stake. Volatile  
60 Organic Compounds are organic compounds, in which hydrogen can be substituted by other compounds  
61 such oxygen, phosphor, or halogens with a vapour pressure superior to 10 Pa in standard conditions (20°C  
62 and 1 atm) (Le Cloirec 1998). These molecules are produced by some process industries, such as refineries,  
63 synthetic flavouring or painting factories (Revah and Morgan-Sagastume 2005), and can also be naturally  
64 generated during biological degradation.

65 VOC can be treated by several methods, including destructive (incineration, biofiltration and catalytic  
66 oxidation) and non-destructive (absorption, adsorption, condensation and membrane filtration) processes.  
67 The selection of the most appropriate method is based on the gas flow rate and the pollutant  
68 concentration (Fig. 1). Absorption is an interesting method, owing to the low pressure drop generated and  
69 the low maintenance needed, contrarily to membrane processes that require high working pressures to  
70 treat low gas flow rates (Fig. 1). An emerging technology like photochemical oxidation shows high efficiency  
71 but is also high energy-consuming; moreover, VOC can be a poison for the catalyst used (Muñoz et al.  
72 2007). Each technology shows limitations and advantages.

73 Hydrophilic compounds like hydrogen sulphide or ammonium are usually treated by chemical scrubbing  
74 (Roustan. 2003; Biard et al. 2009; Biard et al. 2010). Water soluble VOC can also be removed by biological  
75 processes such as biofilters, biotrickling filters or bioscrubbers (Kennes et al. 2009) for low concentrations  
76 and high gas flow rates. Biological treatments have gained support as an effective and economical option  
77 for the treatment of hydrophilic VOC in gas effluents (Burgess et al. 2001).

78 Even if some pollutants such as hydrocarbons, alcohols and esters are consumed by specific microbial  
79 consortium (Ottengraf et al. 1986), several chemical or biological factors can result in an absence of  
80 degradation (Fewson 1991). Owing to VOC toxicity, their concentration in the aqueous phase should be  
81 below the inhibitory threshold for microorganisms. At a chemical level, the shape, the charge or the size of  
82 the molecule, a low concentration and solubility in water or a biosorption phenomenon are factors that can  
83 stave off biodegradation, leading to its classification as a recalcitrant process (Alexander 1973). At a  
84 biological level, the lag-time, the lost of genetic potential or the inability to metabolise pollutants are  
85 factors that can engender non-degradation (Le Cloirec 1998).

86 However, this kind of technology implies an aqueous system containing nutrients (Trinci 1969), which limits  
87 the usefulness of these methods in the case of hydrophobic VOC. Among these latter, dimethyl disulphide  
88 (DMDS) and dimethyl sulphide (DMS) are produced during biological decay, combustion of fossil fuels and  
89 organic matter, as well as sea spray. Both pollutants show low water solubility, 2.5 and 20.5 mg.L-1, a  
90 characteristic odour and low olfactory thresholds: 2.50 and 14.00 µg.m-3 for DMS and DMDS (Hartikainen  
91 et al. 2002). Two main ways are usually selected to remove organic sulphur compounds (hydrophilic and  
92 hydrophobic), the chemical one (charcoal adsorption, incineration and chemical washing) and the biological  
93 one (biodegradation) (Burgess et al. 2001; Cha et al. 1999).

94 Some other compounds are also poorly soluble, for example aromatic compounds, such as toluene. Thus,  
95 chemical techniques are generally preferred for complex VOC mixtures or for products that can be  
96 damaged by strong oxidants (Biard et al. 2010).

97 The aim of this review is to discuss the choice of the most appropriate liquid absorbent to solubilise the  
98 model hydrophobic odorous VOC selected, namely toluene, DMS and DMDS (Table 1). The absorbent  
99 should be biocompatible towards microorganisms and not biodegradable in view of its recycling in the  
100 whole process. The choice of the liquid absorbent as a function of the requirements of each step of the  
101 proposed integrated process is examined in this paper.

## 102 **2. The considered integrated process**

103 In order to remove hydrophobic compounds such as aromatic, sulphur and/or odorous products, a possible  
104 process consists of coupling absorption and biodegradation in a two-phase partitioning bioreactor (TPPB),  
105 allowing the regeneration of the absorbent phase. To increase the gas-liquid mass transfer of hydrophobic  
106 compounds, the absorbent is a non-aqueous phase liquid (Déziel et al. 1999). A schematic approach of the  
107 multistep process is presented in Fig. 2 (Césarío et al. 1998). The first step consists of VOC absorption in a  
108 NAPL and the second of NAPL regeneration by VOC biodegradation (TPPB). Both steps are discussed in this  
109 review to select the most appropriate NAPL. A two steps process is proposed instead of only a TPPB  
110 operation mode involving absorption and biodegradation in the same process unit (such as a stirred tank),  
111 since kinetics of VOC absorption on the one hand and VOC biodegradation on the other hand are expected  
112 to be largely different. The differentiation of the two steps would therefore lead to more flexibility and  
113 would be helpful for the driving of the process and its control.

114 In the integrated process, the target compounds (VOC) are absorbed in an NAPL (Daugulis and Boudreau  
115 2003); after VOC biodegradation in an emulsion organic/aqueous phase, the NAPL can be regenerated and  
116 recycled in the gas-liquid contactor after a separation step from the aqueous phase. The bioreactor is  
117 characterised by a water-immiscible NAPL loaded with VOC and an aqueous phase containing  
118 microorganisms. In other words, VOC-trapping is achieved in an absorption contactor (wherein the NAPL is  
119 the absorbent phase), which is followed by a bioreactor (Daugulis 2001).

120 The NAPL plays two functions:

- 121 • The role of absorbent in the gas-liquid contactor in order to increase mass transfer between the gas  
122 and the liquid phase, since the hydrophobic VOC solubility is more significant in the NAPL than in water.
- 123 • The role of storage phase for toxic or hydrophobic substrates in the bioreactor, allowing maintaining  
124 sub-inhibitory concentrations in the aqueous phase.

125 Several works dealing with two-phase partitioning bioreactor (TPPB) (Déziel et al. 1999; Daugulis 2001;  
126 Yeom and Daugulis 2000; Malinowski 2001; Mahanty et al. 2008) are available in the literature. Since the  
127 mid-seventies, bioconversion of toxic and/or hydrophobic compounds has been investigated in multiphase  
128 bioreactor systems (Table 2).

129 The considered two steps process presents several advantages compared to other biotechnologies  
130 (bioscrubbers or biofilters) (Yeom and Daugulis 2000); advantages and drawbacks are discussed in Table 3.  
131 Among them, biofilters are the most commonly used processes for the removal of gaseous effluents loaded  
132 with low VOC concentrations. For example, total toluene removal ( $164.4 \text{ g.m}^{-3}.\text{h}^{-1}$ ) using a perlite filter bed  
133 involving fungi was recorded (Estévez et al. 2005), whereas Pernafteta-Boldù et al. (Pernafteta-Boldù et al.  
134 2008) recorded a removal efficiency of 62% (corresponding to a removed toluene gaseous flux of  $30 \text{ g.m}^{-3}.\text{h}^{-1}$ ).  
135 Besides, significant DMS (dimethylsulphide) purification capacities were also recorded using biofilters by

136 Zhang et al. (Y. Zhang et al. 2007) ( $0.20 \text{ g DMS.m}^{-3}.\text{h}^{-1}$  or  $0.10 \text{ gS.m}^{-3}.\text{h}^{-1}$ ), and by Shu and Chen (Shu and  
137 Chen 2009) ( $90 \text{ gS.m}^{-3}.\text{h}^{-1}$ ).

138 Similarly to toluene, experimental conditions have also an effect on the removal capacity, namely the  
139 considered microorganisms (fungi, pure culture, mixed culture...), the relative humidity of the gas phase,  
140 the residence time and the environmental conditions.

141 The main downsides of biofiltration are:

- 142 - the long starting period corresponding to cell proliferation in the bed (Daugulis 2001),
- 143 - the sensibility of the process versus a lot of environmental conditions (Kennes et al. 2009),
- 144 - the biofilter volume and hence its built-up area.

145 Water is not an adequate absorbent phase owing to substrate hydrophobicity. Indeed, mass transfer is the  
146 rate-limiting step in biological processes due to the low VOC solubility in water (Césario et al. 1997a).  
147 Therefore, an NAPL can be selected to improve mass transfer (Guieysse et al. 2008) and then to reduce the  
148 residence time in the gas-liquid contactor. Indeed, a large amount of hydrophobic compounds can be  
149 stored in an organic phase, the NAPL, which can be considered as a pollutant tank that can be employed to  
150 release low hydrophobic substrate concentrations or non-toxic inhibitory for cells contained in the aqueous  
151 phase. Moreover, various compounds such as PAH mixture, mutagenic or carcinogenic pollutants,  
152 hydrophobic, toxic products, but also mixtures of hydrophobic and hydrophilic VOC can be treated by this  
153 kind of reactor (Table 2), since the liquid phase can consist of the NAPL alone or a water/NAPL emulsion.

154 In order to optimise the process, many criteria must be taken into account. Among them, the choice of the  
155 organic phase is one of the key factors.

## 156 **3. Absorption of hydrophobic VOC**

### 157 **3.2. Mass transfer theory**

158 The first process step concerns the absorption of hydrophobic VOC in the NAPL. The thermodynamic  
159 equilibrium between the gas and liquid phases, as well as mass transfer kinetics from the gaseous phase to  
160 the liquid phase, has to be considered (F. Heymes et al. 2007; Hernández et al. 2011). Among the various  
161 technical ways usually applied to achieve contact between both phases (gas and liquid), packed columns  
162 can be chosen due to the low pressure drop they imply and the relatively high interfacial area they offer.

163 Absorption requires knowledge of hydrodynamic parameters like pressure drop and liquid hold up. These  
164 variables depend on the geometry of the system (dimensions of the apparatus), the type of column packing  
165 (shape, size, porosity, specific area, etc), the flow rates and the fluid characteristics under the operating  
166 conditions (temperature, pressure, physico-chemical properties, droplet distribution). Once the  
167 hydrodynamic parameters have been selected and optimised, mass transfer considerations must be  
168 discussed.

169 Moreover, the rate-limiting step is the mass transfer rate of hydrophobic gaseous compounds to the  
170 aqueous phase, so that performing the absorption step in a gas-liquid contactor can appear especially  
171 relevant. Owing to the lower Henry's constant of hydrophobic VOC in NAPL than in water, the use of NAPL  
172 instead of water is preferable (Dumont and Delmas 2003).

173 Gas-liquid mass transfer can be described by Eq. 1 (Roustan. 2003).

$$174 \quad \frac{dC_L}{dt} = K_L a (C^* - C_L) \quad (1)$$

175 Where  $C_L$  and  $C^*$  are the VOC concentrations in the liquid phase (NAPL) and in equilibrium with the gas  
176 phase respectively, and  $K_L$  is the overall VOC mass transfer coefficient in the liquid phase.

177 In 1924, Lewis and Whitman described the boundary film model to characterise gas-liquid mass transfer.  
178 Using Eq. 1 describing the physical mass transfer between the gas and the liquid phases and Eq. 2 related to  
179 the mass balance in the packed column, Eq. 3 can be deduced and highlights the mass transfer key factors,  
180 the Henry's constant  $H$  (mol.m<sup>-3</sup> gas/mol.m<sup>-3</sup> liquid), the overall liquid mass transfer coefficient  $K_L$  (m.s<sup>-1</sup>),  
181 and the volumetric interfacial area  $a$  (m<sup>2</sup>.m<sup>-3</sup>).

$$182 \quad Q_G (C_{G,in} - C_{G,out}) = Q_L (C_{L,out} - C_{L,in}) \quad (2)$$

$$183 \quad Q_G (C_{G,in} - C_{G,out}) = K_L a V \Delta C_{ML} = K_L a V \frac{(C_{G,in}/H - C_{L,out}) - (C_{G,out}/H - C_{L,in})}{\ln \left( \frac{C_{G,in}/H - C_{L,out}}{C_{G,out}/H - C_{L,in}} \right)} \quad (3)$$

184 With  $Q_G$  and  $Q_L$  the gas and liquid volumetric flow rates (m<sup>3</sup>.s<sup>-1</sup>), and  $\Delta C_{ML}$ , the average logarithmic  
185 concentration of the pollutant in the liquid phase (mol.m<sup>-3</sup>).

186 Regarding the terms of these equations, it appears that the physical properties of the NAPL and the VOC  
187 (density, viscosity, gas diffusivity and solubility in the liquid phase) influence the performances of  
188 absorption.

189 Owing to the higher hydrophobic VOC solubility in a NAPL than in water, their removal can be significantly  
190 increased due to a higher driving force between gas and NAPL (Césario et al. 1998).

### 191 3.2. Henry's constants

192 Besides hydrodynamic parameters, like gas velocity and column dimensions, mass transfer depends on VOC  
193 equilibrium between both phases and mass transfer velocity. The former factor is linked to VOC solubility in  
194 the NAPL, which can be deduced from the Henry's equation (Eq. 4):

$$195 \quad C_G = H C_L \quad (4)$$

196 With  $C_G$  and  $C_L$  the VOC concentrations in the gas and the liquid phases respectively, and  $H$  the  
197 dimensionless Henry's constant.

198 Hence, the lower the Henry's constant, the better the gas-liquid mass transfer. For hydrophobic VOC, the  $H$   
199 values in water are high owing to their low solubility (Table 4). As a consequence, the amount of VOC likely  
200 to be transferred in the liquid phase is low, and the maximum solubility is rapidly reached, leading to a nil  
201 driving force ( $\frac{C_G}{H} - C_L$ ), so that mass transfer is stopped.

202 If no chemical reaction occurs, a more appropriate absorbent phase must be chosen, *i.e.* a liquid phase in  
203 which Henry's constant values of the targeted hydrophobic VOC are lower. Henry's constant values of  
204 toluene, DMS and DMDS in different NAPL are collected in Table 5, and compared to those in water,  
205 showing the higher affinity of the VOC for NAPL than for water.

206 Darracq et al. (Darracq et al. 2010c) showed that the Henry's constant ( $H''$  in  $\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ ) of DMDS and  
 207 toluene in a silicone oil/water emulsion can be related to the volume fraction of NAPL  $x$  following Eq. 5:

$$208 \frac{1}{H''_{VOC_{emulsion}}} = \frac{1}{H''_{VOC_{Solvent}}} x + \frac{1}{H''_{VOC_{Water}}} (1-x) \quad (5)$$

209 However, experimental values given in Table 6 show that the comparison between 100% NAPL and a  
 210 water/NAPL emulsion is not easy to establish since no clear trend can be deduced. Liquid or pollutant  
 211 properties on one hand and the used gas-liquid contactor system on the other hand most likely account for  
 212 the differences between the considered systems, 100% water, 100% NAPL and water/NAPL emulsion.

### 213 3.3. Global mass transfer coefficient

214 In addition to the Henry's constant, other parameters have an impact on mass transfer. Among them, the  
 215 local liquid and gas mass transfer coefficients ( $k_L$  and  $k_G$ ), as well as the global liquid and gas mass  
 216 transfer coefficients ( $K_L$  and  $K_G$ ). Eqs. 6 and 7 describe the relation between these coefficients (Roustan.  
 217 2003).

$$218 \frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \quad (6)$$

$$219 \frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \quad (7)$$

220 Values of  $K_L a$  are reported in Table 6, allowing the comparison between absorption in water and in NAPL.  
 221 Variations of  $K_L a$  values can be observed, depending on the hydrodynamic conditions and the design of  
 222 the gas-liquid contactor used (Bourgeois et al. 2009). Nevertheless, whereas Bourgeois et al. (Bourgeois et al.  
 223 2009) worked with a cables-bundle scrubber, while other authors (Dumont et al. 2006; Darracq et al.  
 224 2010c) used a bubble batch reactor, very close mass transfer values were obtained.

225 However, few data concerning toluene, DMS or DMDS are available in the literature.  $K_L a$  values have been  
 226 also measured in water/NAPL emulsions (Césario et al. 1997a; Rodriguez et al. 2001; Clarke and Correia  
 227 2008). Previous works dealing with oxygen mass transfer in water/NAPL emulsions showed that the volume  
 228 fraction of NAPL in the emulsion have an effect on  $K_L a$  values (MacMillan and Wang 1987; Rols et al. 1990;  
 229 Césario et al. 1997a; Dumont et al. 2006; Quijano et al. 2010b).

### 230 3.4. Diffusion coefficient

231 In addition to the Henry's constants, two parameters have an impact on the global mass transfer  
 232 coefficient, the film thickness and the diffusion coefficient. Whatever the theoretical model, film,  
 233 penetration or surface-renewal theories, Dumont and Delmas (Dumont and Delmas 2003) showed that the  
 234 VOC diffusion coefficient ( $D_L$ ) is an important parameter. According to Heymes et al. (F Heymes et al.  
 235 2006), the diffusion coefficient has a strong influence on absorption efficiency. In short, the diffusion  
 236 coefficient in the liquid absorbent is a key parameter to understand complex mass transfer phenomena and  
 237 to design mass transfer devices.



238 In 2001, Fei and Bart (Fei and Bart 2001) used the group contribution method to determine this coefficient.  
239 However, this method gives reliable results only for binary and low viscous systems. Bourgois et al.  
240 (Bourgois et al. 2009) showed that some widely used empirical correlations, like the Scheibel's correlation  
241 (Scheibel 1954) and the Wilke and Chang's correlation (Wilke and Chang 1955), are inappropriate for the  
242 estimation of liquid diffusivities in viscous solvents. The results displayed in Table 7 concern mainly toluene,  
243 while there is a lack of information dealing with volatile sulphur compounds. Liquid diffusivities in some  
244 organic solvents are often ten times lower than in water.

### 245 **3.5. NAPL viscosity**

246 In addition to the diffusion coefficient, the NAPL viscosity plays a role on the hydrodynamic behaviour of  
247 the column, on the diffusion coefficient of the selected VOC. This parameter influences hydrodynamics and  
248 gas-liquid mass transfer. A low viscosity minimises the thickness of the interface between both phases and  
249 increases the diffusion kinetics in this layer (F Heymes et al. 2006). Moreover, viscosity has an effect on the  
250 Henry's constant (Table 5). Indeed, for a given temperature, an increase of the viscosity results in an  
251 increase of the Henry's constant.

252 To conclude on these considerations, the physico-chemical properties of the NAPL play a role on  
253 hydrodynamics (viscosity for example) and hence on mass transfer coefficients (absorption capacity and  
254 absorption rate). The selected NAPL should therefore comply with the following criterion, a low Henry's  
255 constant of the considered VOC.

## 256 **4. Regeneration of the Non-Aqueous Phase Liquid by** 257 **biodegradation**

### 258 **4.1. Two-phase partitioning bioreactor (TPPB)**

259 After VOC mass transfer from the gas phase to a NAPL, VOC degradation is carried out in a two-phase  
260 partitioning bioreactor (TPPB), which consists of a stirred bioreactor filled with two immiscible liquid  
261 phases, leading to the formation of an emulsion, increasing the interfacial area. This concept is based on  
262 the selective partitioning of the pollutant between water and NAPL. VOC biodegradation performances  
263 depend on the presence and the assimilation potential of various microbial agents such as bacteria, fungi or  
264 yeasts in the aqueous phase (Rehmann and Daugulis 2007). In a TPPB, hydrophobic (or toxic) compounds  
265 are delivered to the aqueous phase at sub-inhibitory levels for microorganisms in case of toxic compounds  
266 or at the solubilisation limit in case of hydrophobic compounds, related to the microbial demand.

267 Déziel et al. (Déziel et al. 1999) proposed three mechanisms for hydrophobic or toxic compounds  
268 consumption:

- 269 1. The substrate is removed after its solubilisation in an aqueous phase. The degradation rate is function  
270 of the mass transfer rate from the organic to the aqueous phase. Efrogmson and Alexander (Efrogmson  
271 and Alexander 1991) as well as Bouchez et al. (Bouchez et al. 1997) showed that VOC biodegradation  
272 rate in the organic phase is higher than mass transfer rate between both phases. Therefore,  
273 biodegradation only occurs in the aqueous phase and is governed by substrate equilibrium between  
274 both liquid phases.

- 275 2. VOC removal takes place at the liquid-liquid (organic-aqueous) interface. VOC can be directly  
276 assimilated at the interface after biofilm development between both liquid phases (Guieysse et al.  
277 2001). Muñoz et al. (Muñoz et al. 2006) showed that cells are in direct contact with the organic phase  
278 since VOC concentration is more significant near the interface. This phenomenon was confirmed by  
279 Efroymson and Alexander (Efroymson and Alexander 1991) who reported bacterial accumulation at the  
280 interface and a decrease of cell growth in the aqueous phase.
- 281 3. If the microorganisms are surfactant- or emulsifier-producers, there is formation of small droplets or  
282 micelles, leading to a reduction of the surface tension of the aqueous phase and an increase of the  
283 interfacial area until microemulsion formation (Desai and Banat 1997). This phenomenon improves  
284 substrate availability for microorganisms mainly located at the organic-aqueous interface and hence  
285 improves VOC removal.

286 Some interactions can be considered as key factors in the process, like VOC / NAPL, NAPL / microorganisms,  
287 or water / VOC. Some authors consider that TPPBs should be used with microorganisms able to consume  
288 pollutants directly at the NAPL-water interface (Guieysse et al. 2001). This interfacial area has a significant  
289 role in the uptake mechanism. Indeed, Ascon-Cabrera and Lebeault (Ascon-Cabrera and Lebeault 1995)  
290 showed that the degradation rate increases after cell adhesion to the interface of NAPL, *i.e.* when the  
291 interfacial area increases. This parameter, which can be considered as a key factor in the liquid-liquid mass  
292 transfer step, is affected by the operating conditions like the stirring speed and the type of impeller (if  
293 used), the volume fraction of NAPL in the emulsion, or the presence of possible chemical reactions in the  
294 aqueous phase. For instance, MacLeod and Daugulis (MacLeod and Daugulis 2005) showed an increase of  
295 the rate of PAH (Polycyclic Aromatic Hydrocarbon) degradation linked to an increase of the stirring speed  
296 (84 and 150 mg.L<sup>-1</sup>.day<sup>-1</sup> at 300 and 500 rpm respectively). These authors also proved that oxygen is not the  
297 limiting factor in the degradation step (MacLeod and Daugulis 2005), even if this assessment should be  
298 considered with caution, since it is most likely related to VOC concentration and VOC Henry's constant.  
299 Otherwise, Ascon-Cabrera and Lebeault (Ascon-Cabrera and Lebeault 1993) showed that the NAPL volume  
300 in the emulsion has a significant effect on the microorganism growth; for a silicone oil/water system the  
301 highest specific growth rates are recorded for stirring speed ranging between 500 and 700 rpm and a  
302 volume fraction of NAPL ranging from 20 to 40%.

303 There is a general agreement that the major part of hydrophobic VOC uptake is achieved at the interface of  
304 both liquid phases due to the adherence of cells at the interface (Ascon-Cabrera and Lebeault 1993; Déziel  
305 et al. 1999; Muñoz et al. 2006). The following steps can be considered during hydrophobic pollutant  
306 removal in a TPPB (Déziel et al. 1999):

- 307 1. The substrate is consumed in the aqueous phase.
- 308 2. After an increase of the biomass, cells become more hydrophobic and can adhere to the NAPL-water  
309 interface where substrate concentration is more abundant.
- 310 3. Then, cell growth and attach at the interface, namely on the NAPL droplet surface. The substrate  
311 amount in the aqueous phase is nil when the biodegradation rate at the interface is higher than the  
312 mass transfer rate.
- 313 4. In addition to biomass growth, substrate consumption can induce biosurfactant production, which  
314 decreases the surface tension and increases the interfacial area. This phenomenon has an effect on the  
315 microorganism growth and the mass transfer rate.
- 316 5. Finally, a stable emulsion (small droplets of NAPL in water) appears, driving to high mass transfer  
317 performances.

318 Besides pollutants should be metabolised by activated sludge, the system should fulfil several  
319 characteristics. A method for the choice of the most appropriate NAPL to be implemented in a TPPB has

320 been proposed by several authors. The NAPL should be water-immiscible, safe, chemically stable,  
 321 biocompatible (non-toxic towards the microbial community), non-biodegradable and should not have a too  
 322 high specific VOC partition coefficient between NAPL and water (Déziel et al. 1999; Muñoz et al. 2006;  
 323 Bruce and Daugulis 1991; Quijano et al. 2009). Experiments carried out with various microorganisms and  
 324 NAPL are listed in Table 8. These different parameters are discussed hereafter.

#### 325 **4.2. Toxicity of NAPL towards microorganisms or biocompatibility**

326 The metabolic activity of microorganisms regulates the mass transfer rate from the organic phase to the  
 327 aqueous phase or in other words, this system is self-regulatory (Collins and Daugulis 1997b). The NAPL  
 328 should not interfere in the system, but improve mass transfer and biodegradation rate.

329 Otherwise, the NAPL should not be toxic towards microorganisms. The literature relates that NAPL  
 330 preferentially accumulates on the cytoplasmic membrane of cells and causes damages, resulting in the  
 331 destruction of the microorganism; the accumulation of lipophilic compounds in the membrane has  
 332 considerable effects on its structural and functional properties (De Bont 1998; Sardesai and Bhosle 2002).  
 333 According to Brink et al. (Brink et al. 1988) changes in permeability, enzyme inhibition, protein deactivation,  
 334 or a breakdown of transport mechanisms can be observed after contact between microorganisms and a  
 335 NAPL.

336 In order to examine the growth-potential of microorganisms in the presence of the NAPL, two parameters  
 337 are commonly taken into account, NAPL polarity and NAPL solubility in water, through the octanol/water  
 338 partition coefficient  $P$  or  $Kow$  (Bruce and Daugulis 1991; Ogino et al. 1999) (Eq. 8):

$$339 \quad \log Kow = \log P = \log \left( \frac{[Solvent]_{Octanol}}{[Solvent]_{water}} \right) \quad (8)$$

340 The partition coefficients of several NAPL that can be implemented in two-phase partitioning bioreactors  
 341 are collected in Table 9.

342 Log  $Kow$  characterizes the resistance of microorganisms, and below a critical log  $Kow$  value, growth cannot  
 343 occur (Table 10). This parameter is commonly accepted as the best indicator of NAPL biocompatibility  
 344 (Laane et al. 1985; Laane et al. 1987; Inoue and Horikoshi 1991).

345 For instance, *Pseudomonas aeruginosa* LST-03 can grow in the presence of various NAPL having log  $Kow$   
 346 superior to 2.9 (critical value of log  $Kow$ ). Indeed gram-negative bacteria like the *Pseudomonas* genus are  
 347 assumed to be more NAPL tolerant than gram-positive bacteria. This resistance can be explained by the  
 348 presence of an additional outer membrane made up of phospholipids and lipopolysaccharides if compared  
 349 to gram-positive bacteria (Sardesai and Bhosle 2002). The presence of the NAPL in the lipid bilayer results  
 350 in an increase of the fluidity leading to an inactivation of the membrane-embedded proteins, such as ion  
 351 pumps and ATPases, or an increase of the membrane permeability, which is considered as the main reason  
 352 for cell death (Heipieper et al. 2007; Osborne et al. 1990; Sikkema et al. 1995). The relationship linking the  
 353 partition coefficient and biocompatibility is based on the assumption that the octanol/water system  
 354 provides an adequate description of the hydrophobic interactions occurring in a biological system (Bruce  
 355 and Daugulis 1991).

356 There is a general agreement that the log  $K_{ow}$  critical value is 4.0 to determine the biocompatibility, while  
 357 below this value the NAPL is toxic towards most of the microorganisms (Déziel et al. 1999; Arriaga et al.  
 358 2006; Collins and Daugulis 1997a, 1999a; Hayachi et al. 2003; Matsumoto et al. 2004).

359 According to their toxicity, a lot of NAPL can be used in a TPPB containing pure cultures (autotrophic and  
 360 heterotrophic microorganisms) or mixed cultures including activated sludge.

### 361 4.3. Miscibility of NAPL in water

362 **The NAPL miscibility in water should be the lowest possible in view of a readily separation in the**  
 363 **subsequent settler. The addition of an immiscible phase leads to an emulsion, resulting in an increase of**  
 364 **the interfacial area and hence enhances VOC transfer to the aqueous phase. However, one of the**  
 365 **drawbacks of the process is a possible biosurfactants production, which can induce an increase of**  
 366 **emulsion stability and hence more difficulties to recover the organic phase during the separation step. A**  
 367 **low NAPL solubility would also allow to limit the effects of potential toxicity towards**

### 368 4.4. Biodegradability of NAPL

369 In view of their recycling, biodegradable NAPL should be avoided while it is the case for most of them  
 370 (Table 9).

371 Table 9 highlights the difficulty to select a non-biodegradable NAPL. Van der Meer et al. (Van der Meer et  
 372 al. 1992) indicated that in the presence of a microbial consortium, a limited number of NAPL can be chosen.  
 373 Indeed, after a lag (or adaptation) time, almost all the organic compounds are attacked by microorganisms.  
 374 Muñoz et al. (Muñoz et al. 2007) consider that it is difficult to predict the stability of a given NAPL in the  
 375 presence of microorganisms on long-term, owing to a possible emergence of microorganisms able to  
 376 degrade the NAPL. Besides its recycling is no longer possible, NAPL biodegradability can lead to a  
 377 competition between substrates, the NAPL and VOC.

### 378 4.5. Parameters characteristic of liquid-liquid VOC mass transfer in TPPB

379 Since biodegradation occurs in the aqueous phase, mass transfer between the NAPL and the aqueous  
 380 phase is an important parameter. Several authors studied mass transfer between a gas phase and a water/  
 381 NAPL mixture (Césario et al. 1998; Muñoz et al. 2007; Dumont et al. 2006). The concentration gradient  
 382 between both phases can be described using Eq. 1 and Fig. 3. However, the interface concentration ( $C^*$ )  
 383 cannot be measured, and hence is deduced from the specific VOC partition coefficient (Césario et al. 1997a;  
 384 Tudose and Apreotesei 2001; Yeom and Daugulis 2001a) (Eqs. 9 and 10):

$$385 \frac{dC_{NAPL}}{dt} = K_{NAPL}^{NAPL/W} a \left( C_{NAPL} - K_{NAPL/W} C_{water} \right) \text{ (NAPL side)} \quad (9)$$

$$386 \frac{dC_{water}}{dt} = K_{water}^{NAPL/W} a \left( \frac{C_{NAPL}}{K_{NAPL/W}} - C_{water} \right) \text{ (Water side)} \quad (10)$$

387 Where  $C_{NAPL}$  and  $C_{water}$  are the VOC concentrations in the NAPL and in water respectively,  $K_{NAPL}^{NAPL/W}$  and  
 388  $K_{water}^{NAPL/W}$  are the global mass transfer coefficients of VOC ( $m \cdot s^{-1}$ ) in the NAPL and in water respectively  
 389 ( $mol \cdot m^{-3}$ ),  $K_{NAPL/W}$  is the specific VOC partition coefficient between the NAPL and water (dimensionless),  
 390 and  $a$  is the volumetric interfacial area ( $m^2 \cdot m^{-3}$ ).

391 Obviously, the global mass transfer coefficient and the volumetric interfacial area should be as high as  
 392 possible to increase mass transfer in the aqueous phase.

393 A specific VOC partition coefficient can be defined by the NAPL on water VOC concentration ratio (Eq. 11),  
 394 and should be as high as possible to obtain the highest concentration gradient. Various coefficients for  
 395 toluene partition between various NAPL and water are collected in Table 11:

$$396 \quad K_{NAPL/W} = \frac{[VOC]_{NAPL}}{[VOC]_{Water}} \quad (11)$$

397 Owing to the low aqueous VOC solubility, a maximum VOC concentration in water is rapidly reached,  
 398 leading to the cessation of VOC mass transfer. However, mass transfer between both liquid phases (NAPL  
 399 and water) is controlled by the VOC biodegradation in the aqueous phase.

400 The determination of the VOC concentration in the aqueous phase containing microorganisms is given by  
 401 the following relation (Eq. 12):

$$402 \quad \frac{dC_{Water}}{dt} = K_{Water}^{NAPL/W} a \left( \frac{C_{NAPL}}{K_{NAPL/W}} - C_{Water} \right) - q_S x' \quad (12)$$

403 Where  $q_S$  is the specific substrate uptake rate and  $x'$  the biomass concentration.

404 Several authors showed the importance of the interfacial area in VOC biodegradation in a TPPB (Ascon-  
 405 Cabrera and Lebeault 1993, 1995; Nakahara et al. 1977; Woodley et al. 1991). Besides, some other  
 406 parameters such as the stirring speed, the interfacial tension of the NAPL and the NAPL/water ratio in the  
 407 bioreactor have an impact on the interfacial area. For instance, Ascon-Cabrera and Lebeault (Ascon-Cabrera  
 408 and Lebeault 1995) showed that the NAPL/water ratio in a TPPB plays a role on the interfacial area when  
 409 this ratio increases up to 40%. A NAPL on water ratio in the range of 20 – 30% was found to be the most  
 410 efficient for some VOC biodegradation (Darracq et al. 2012). The low biological activity outside this range  
 411 (less than 20% or more than 30%) can be explained by interfacial area phenomena, since for a small  
 412 proportion of oil, the emulsion is homogeneous but the interfacial area is small; while for high ratios, the oil  
 413 is not completely emulsified and hence mass transfer appears limiting leading to a decreasing substrate  
 414 availability.

## 415 5. Screening and choice of the NAPL

416 In view of process optimisation, the intrinsic NAPL properties should also be considered. Indeed, the NAPL  
 417 should not add pollution, must be non-flammable, and its chemical and thermal properties must fulfil those  
 418 required with the aim of its recycling (Bruce and Daugulis 1991). The NAPL must be a weakly viscous liquid

419 in a range of temperature between 5 and 40°C. To make the separation from water after biodegradation  
420 step feasible, NAPL leading to stable emulsions should be avoided.

421 The literature concerning NAPL density reports that a high density would increase the pressure drop and  
422 hence the operation cost. On the other hand, density should differ from that of water in order to improve  
423 the separation step (in the settler).

424 A lot of significant parameters have to be considered for the choice of an adequate NAPL for the process  
425 coupling absorption and biodegradation. However, each system is specific due to the large number of NAPL  
426 available and the various microorganisms used.

427 All the collected NAPL have been previously used either in a two-phase partitioning bioreactor or as  
428 absorbents in a gas-liquid contactors (scrubber, airlift, bubble column, etc). Among them, a large number  
429 are biodegradable since after an acclimation time, bacteria are able to assimilate these compounds,  
430 particularly alkanes, ketones or hydroxylated NAPL (carboxylic acid, aldehydes, etc). NAPL containing long  
431 alkyl chains or alcohol, ester or carboxylic groups are also biodegradable, and are precursors of beta  
432 oxidation. Other NAPL like phthalates or plasticiser compounds (for example adipates) can also be  
433 degraded by various microorganisms such as *Rhodococcus* or *Sphingomonas* (Nalli et al. 2006; Liang et al.  
434 2008).

435 However, various authors showed that biodegradability decreases with the presence of long alkyl chains or  
436 hydroxyl, ester and acid groups in the molecule (Muñoz et al. 2006; Déziel et al. 1999). Previously,  
437 Alexander (Alexander 1973) reported that a high molecular weight compound, with lot of ramifications, is  
438 biologically recalcitrant. Besides, the type, the number, and the position of the substitutes on simple  
439 organic molecules influence their biodegradability. For instance, the substitution of a hydrogen atom by  
440 chlorine decreases the biodegradability of the molecule. Various compounds having a very low degradation  
441 rate or a total refractory towards microorganism are described as bio-recalcitrant. However, recalcitrance is  
442 not enough for the proposed process since it means a biodegradation of the considered NAPL after an  
443 acclimation time.

444 According to Ascon-Cabrera and Lebeault (Ascon-Cabrera and Lebeault 1993, 1995) and Déziel et al. (Déziel  
445 et al. 1999), four kinds of NAPL are potentially non-biodegradable:

- 446 • HMN (2,2,4,4,6,8,8-Heptamethylnonane) owing to the presence of terminal methyl groups. Some  
447 authors showed the resistance of HMN to biodegradation by *Arthrobacter* (Efroymsen and Alexander  
448 1991) or mixed cultures (Ghoshal et al. 1996; Kirkwood et al. 2008); while marine microbial community  
449 would be able to degrade HMN (Rontani and Giusti 1986).
- 450 • Fluorocarbon FC 40 has been tested by Césarío et al. (Césarío et al. 1998), who could not put its  
451 biodegradation in evidence. However, recent reports questioned on the high volatility of this compound  
452 and its high power of depletion on ozone (Quijano et al. 2009).
- 453 • Polymers are potentially usable in a TPPB. The polyisobutylene is recalcitrant towards microorganisms  
454 (Alexander 1973) since constituted of many terminal methyl groups. However, the viscosity of this  
455 polymer is high and will increase the pressure drop in the gas/liquid contactor, and/or the stirred power  
456 needed in order to create a maximal interfacial area to improve the transfer in the aqueous phase. In  
457 this case, the process consumes a large amount of energy.

- 458 • Silicone oil (polymethylsiloxane or PDMS) has been used by several authors (Ascon-Cabrera and  
459 Lebeault 1993, 1995; Bouchez et al. 1995; Gardin et al. 1999; Fazaelpoor and Shojaosadati 2002; Aldric  
460 et al. 2009a) as an absorbent and a pollutant tank in a multiphase bioreactor. Among the various  
461 polymers of this family, all are potentially usable as NAPL in TPPB, owing to their commonly accepted  
462 absence of biodegradability. They should be, however, considered with circumspection due to the  
463 following general features, a high viscosity and a solid state at ambient temperature.
- 464 • The last class of compounds concerns ionic liquids (IL), which are more or less biodegradable, depending  
465 on their structure.

466 Besides NAPL biodegradability, other parameters such as viscosity, toxicity to humans and the environment  
467 refine the choice and lead to the elimination of many NAPL.

468 Finally, all organic solvents such as alkanes, alkynes, carboxylic acids, phtalates, plasticiser compounds... are  
469 not usable in TPPB because they are easily metabolized by microorganisms. Among the remaining solvents,  
470 HMN is a recalcitrant compounds with terminal methyl groups; however, it is biodegradable after a long  
471 contact-time with some bacterial agents, while trihexylamine and fluorocarbons cannot be selected  
472 because of their toxicity toward humans or the environment. Among the above solvents, only silicone oils  
473 and ionic liquids appear therefore really relevant. Their main characteristics are presented thereafter.

## 474 5.1. Silicone oils

475 These oils were synthesized for the first time in 1870. They found an important development due to their  
476 physicochemical properties and their physical structure, since they consist of the repetition of a Si-O-Si  
477 group. Silicone oils present a good thermal resistance and an excellent chemical inertia facing hydrolysis or  
478 oxidation, due to the stability and the strength of the Si-O-Si bonds. Various functional groups can be linked  
479 to the silicon atom, leading to several available silicone oils (Fig. 4a) with various viscosities. Finally, the  
480 physicochemical properties of these oils are very interesting, for example their superficial tensions are  
481 about  $20 \text{ mN.m}^{-1}$ ; it should be remembered that the value for water is  $73 \text{ mN.m}^{-1}$ . From an environmental  
482 point of view, this oil (PDMS) is persistent because it does not bioaccumulate, to adsorb to suspended  
483 particle matter (Nendza 2007).

484 More specifically for hydrophobic VOC removal, among the available silicone oils, polydimethylsiloxane  
485 (Fig. 4a) appears as an interesting candidate, since it is biocompatible and non-biodegradable. Some studies  
486 reported in Table 12 confirm the relevance of PDMS as a NAPL for the proposed process, namely a tank for  
487 hydrophobic or toxic compounds (VOC or PAH) before subsequent biodegradation.

488 In addition to the high solubility of hydrophobic compounds in PDMS, oxygen is seven times more soluble  
489 in silicon oil than in water. In the case of the differentiation of the two steps, absorption and  
490 biodegradation, oxygen supply by bubbling is not required in TPPB since a large amount of oxygen present  
491 in the oil is available for micro-organisms growth. The kinetics of degradation is not limited by a lack of  
492 oxygen.

493 In this kind of bioreactors, several authors working with silicone oil (Ascon-Cabrera and Lebeault 1993;  
494 Osswald P. et al. 1996) noticed a modification of bacterial behaviour due to cell adhesion to the oil leading  
495 to a higher interfacial area; the consequence is a more important dispersion of the NAPL and hence an  
496 increase of substrate bioavailability. Moreover, using a water/PDMS two-phase system with activated

497 sludge, Ascon-Cabrera and Lebeault (Ascon-Cabrera and Lebeault 1993) showed that the microbial activity  
498 (growth rate) increases and the lag time decreases compared to a monophasic aqueous system.

499 Another positive aspect of silicone oil is their biocompatibility for bacterial agents (Darracq et al. 2010c;  
500 Darracq et al. 2010a). A large number of bacteria, fungi or microorganisms have the ability to grow in the  
501 presence of silicone oil. Enzymes have been also successfully implemented in TPPB containing silicone oil to  
502 treat recalcitrant compounds, like anthracene (Eibes et al. 2007); a nearly complete anthracene oxidation  
503 was reached using an enzyme peroxidase.

504 Silicone oil seems therefore the most appropriate NAPL for TPPB.

505 Concerning the absorption step, PDMS shows interesting physico-chemical properties such as high VOC  
506 affinity (Henry's constants) and high mass transfer coefficients. For example, Aldric et al. (Aldric et al.  
507 2009b) showed that the addition of 10% PDMS in water increases the mass transfer coefficient of oxygen  
508 and isopropylbenzene by 20%. Moreover, these results were confirmed by other authors (Dumont and  
509 Delmas 2003; Darracq et al. 2010c). Indeed, the latter authors showed that for a low added amount of  
510 PDMS in water, the Henry's constants for hydrophobic VOC decrease rapidly. The relevance of silicon oil for  
511 the absorption step is therefore confirmed.

## 512 **5.2. Ionic liquids**

513 These compounds are considered as "green solvents" because they present highly relevant  
514 physicochemical properties for environmental applications, especially their low vapour pressure.

515 Ionic liquids are organic salts consisting of two parts, an organic positive ion like imidazolium (Fig. 4b) and a  
516 negative ion, namely the counter-ion, leading to a neutral compound (Table 13) (Yang and Pan 2005). Ionic  
517 liquids represent an interesting alternative in various processes (Diels-Alder or Fridel-Crafts reactions, as  
518 solvent in liquid-liquid extractions, etc) compared to common organic solvents (methanol, ethanol, etc)  
519 (Welton 1999; Docherty and Kulpa 2005). These compounds are also used as media to perform biocatalytic  
520 reactions. For instance, Zhang et al. (F. Zhang et al. 2008) used BmimPF<sub>6</sub> (1-Butyl-3-methylimidazolium  
521 hexafluorophosphate) in a two-phase system (IL/water) to carry out a reduction reaction in the presence of  
522 a pure bacterial culture of *Aureobasidium pullulans*.

523 Most of the ILs present a low vapour pressure, a low melting point, a high polarity. They are liquid at room  
524 temperature, non-flammable, chemically and thermally stable. However, their properties depend on their  
525 structure. The effects of positive and negative ions on IL properties are collected in Table 14. Hence, the  
526 cation and the anion are selected according to the chemical properties aimed. Therefore, among the  
527 various available ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF<sub>6</sub>) and 1-butyl-3-  
528 methylimidazolium Bis[(trifluoromethyl)sulfonyl]amide seem to be the most relevant for the considered  
529 process (Quijano et al. 2011a, 2011b). Unfortunately, the literature dealing with physico-chemical  
530 properties linked to absorption, like the Henry's constant values for toluene, or other hydrophobic VOC, as  
531 well as their toxicity towards activated sludge and human beings, is scarce.

532 Although IL toxicity represents a key drawback for their full implementation in bioreactors, their flexible  
533 nature is probably the most promising characteristic of these solvents. The possibility to fine-tune  
534 practically all the IL physicochemical properties by modifying the alkyl chain or the anion/cation identity



535 while conserving key properties such as non-volatility, non-flammability and thermal stability can be  
536 considered as an advantage of ILs over traditional solvents (Quijano et al. 2010a).

## 537 **6. Conclusion**

538 The use of a non-aqueous phase liquid (NAPL) can be helpful to remove hydrophobic (or toxic) compound  
539 by absorption. Given that organic compounds are more expensive than water commonly employed in  
540 absorption processes and can be harmful for environment, its recycling must be envisaged. NAPL reuse can  
541 be performed after VOC biodegradation. The choice of the NAPL must therefore fulfill several conditions.  
542 Numerous authors have examined such processes, mainly two-phase partitioning bioreactors, namely  
543 coupling absorption and biodegradation in the same reactor. A large number of organic solvents have been  
544 tested in various experimental conditions, with biodegradation conducted in both pure and mixed cultures;  
545 many criteria appear relevant, depending on the target application.

546 Concerning the absorption step, Henry's constants of VOC in a specific NAPL as well as the NAPL viscosity  
547 proved to be key parameters. The VOC solubility in the NAPL should be as high as possible. The viscosity has  
548 a negative effect on pressure drop in the gas-liquid contactor and on VOC diffusion, and hence on mass  
549 transfer from the gas phase to the NAPL phase. Regarding biodegradation, several parameters must be  
550 considered. The non-biodegradability of the selected NAPL is crucial, but its biocompatibility and an  
551 absence of toxicity towards microorganisms are also relevant.

552 Taking into account all these parameters, silicone oils seem to be the most appropriate NAPL for the  
553 proposed integrated process. They are non-biodegradable, biocompatible with most of the  
554 microorganisms, can be weakly viscous, are efficient absorbents for hydrophobic VOC, have a good  
555 partition coefficient for water and promote gas-liquid mass transfer.

556 Otherwise, even if only few data on their long time behaviour are available, the potentialities of ionic  
557 liquids should be more deeply investigated.

558 All these considerations will be helpful in order to design and optimize a sustainable, performing, cheap  
559 and compact process coupling absorption and biodegradation for VOC removal.

560

561 **References**

- 562 Abe, A., Inoue, A., Usami, R., Moriya, K., & Horikoshi, K. (1995). Degradation of polyaromatic hydrocarbons by  
563 organic solvent-tolerant bacteria from deep sea. *Bioscience Biotechnology and Biochemistry*, *59*, 1154-1156.
- 564 Abed, R. M. M., & Köster, J. (2005). The direct role of aerobic heterotrophic bacteria associated with cyanobacteria in  
565 the degradation of oil compounds. *International Biodeterioration and Biodegradation*, *55*, 29-37.
- 566 Aldric, J. M., Gillet, S., Delvigne, F., Blecker, C., Lebeau, F., Wathelet, J. P., et al. (2009a). Effect of surfactants and  
567 biomass on the gas/liquid mass transfer in an aqueous-silicone oil two-phase partitioning bioreactor using  
568 *Rhodococcus erythropolis* T902.1 to remove VOCs from gaseous effluents. *J. Chem. Technol. Biotechnol.*, *84*,  
569 1274-1283.
- 570 Aldric, J. M., Lecomte, J. P., & Thonat, P. (2009b). Study on mass transfer of isopropylbenzene and oxygen in a two-  
571 phase partitioning bioreactor in the presence of silicone oil. *Appl. Biochem. Biotechnol.*, *153*, 67-79.
- 572 Aldric, J. M., & Thonart, P. (2008). Performance of a water/silicone oil two-phase partitioning bioreactor using  
573 *Rhodococcus erythropolis* T902.1 to remove volatile organic compounds from gaseous effluents. *J. Chem.*  
574 *Technol. Biotechnol.*, *83*, 1401-1408.
- 575 Alexander, M. (1973). Non-biodegradable and other recalcitrant molecules. *Biotechnol. Bioeng.*, *15*, 611-647.
- 576 Alvarez, P. J., & Vogel, T. M. (1991). Substrate interactions of benzene, toluene, and para-xylene during microbial  
577 degradation by pure cultures and mixed culture aquifer slurries. *Appl. Environ. Microbiol.*, *57*(10), 2981-2985.
- 578 Arriaga, S., Muñoz, R., Hernandez, S., Guieysse, B., & Revah, S. (2006). Gaseous hexane biodegradation by *Fusarium*  
579 *solani* in two liquid phase packed-bed and stirred tank bioreactors. *Environ. Sci. Technol.*, *40*, 2390-2395.
- 580 Ascon-Cabrera, M. A., & Lebeault, J. M. (1993). Selection of xenobiotic-degrading microorganisms in a biphasic  
581 aqueous-organic system. *Appl. Environ. Microbiol.*, *59*, 1717-1724.
- 582 Ascon-Cabrera, M. A., & Lebeault, J. M., . (1995). Cell hydrophobicity influencing the activity/stability of xenobiotic-  
583 degrading microorganisms in a continuous biphasic aqueous-organic system. *J. ferment. Bioeng.*, *80*, 270-275.
- 584 Barnabe, E. S., Beauchesne, I., Cooper, D. G., & Nicell, J. A. (2008). Plasticizers and their degradation products in the  
585 process streams of a large urban physicochemical sewage treatment plant. *Water Res.*, *42*, 153-162.
- 586 Berekaa, M. M., & Steinbüch, A. (2000). Microbial Degradation of the Multiply Branched Alkane 2,6,10,15,19,23-  
587 Hexamethyltetracosane (Squalane) by *Mycobacterium fortuitum* and *Mycobacterium ratisbonense*. *Appl.*  
588 *Environ. Microbiol.*, *66*, 4462-4467.
- 589 Biard, P. F., Couvert, A., Renner, C., & Levasseur, J. P. (2010). Wet scrubbing intensification applied to hydrogen  
590 sulphide removal in waste water treatment plant. *Can. J. Chem. Eng.*, *88*, 682-687.
- 591 Biard, P. F., Couvert, A., Renner, C., Zozor, P., Bassivière, S., & Levasseur, J. P. (2009). Hydrogen sulphide removal in  
592 waste water treatment plant by compact oxidative scrubbing in Aquilair Plus™ process. *Water Practice*  
593 *Technol.*, *4*, doi:10.2166/wpt.2009.2023.
- 594 Birman, I., & Alexander, M. (1996). Optimizing biodegradation of phenanthrene dissolved in nonaqueous-phase  
595 liquids. *Appl. Microbiol. Biotechnol.*, *45*, 267-272.
- 596 Bouchez, M., Blanchet, D., & Vandecasteele, J. P. (1995). Substrate availability in phenanthrene biodegradation by  
597 natural microbial communities. *Appl. Microbiol. Biotechnol.*, *43*, 952-960.
- 598 Bouchez, M., Blanchet, D., & Vandecasteele, J. P. (1997). An interfacial uptake mechanism for the degradation of  
599 pyrene by *Rhodococcus* strain. *Microbiol.*, *143*, 1087-1093.
- 600 Boudreau, N. G., & Daugulis, A. J. (2006). Transient performance of two phase partitioning bioreactor treating a  
601 toluene contaminated gas stream. *Biotechnol. Bioeng.*, *94*, 448-457.
- 602 Bourgois, D., Thomas, D., Fanlo, J. L., & Vanderschuren, J. (2006). Solubilities at High Dilution of Toluene,  
603 Ethylbenzene, 1,2,4-Trimethylbenzene, and Hexane in Di-2-ethylhexyl, Diisohexyl, and Diisononyl  
604 Phthalates. *J. Chem. Eng. Data*, *51*, 1212-1215.
- 605 Bourgois, D., Vanderschuren, J., & Thomas, D. (2009). Study of mass transfer of VOCs into viscous solvents in a pilot-  
606 scale cables-bundle scrubber. *Chem. Eng. J.*, *145*, 446-452.
- 607 Brink, L. E. S., Tramper, J., Luyben, K. C. A. M., & Van 't Riet, K. (1988). Biocatalysis in organic media. *Enzyme*  
608 *Microb. Technol.*, *10*, 743-736.
- 609 Bruce, L. J., & Daugulis, A. J. (1991). Solvent selection strategies for extractive biocatalysis. *Biotechnol. Prog.*, *61*,  
610 116-124.
- 611 Burgess, J. E., Parsons, S. A., & Stuetz, R. M. (2001). Developments in odour control and waste gas treatment  
612 biotechnology: a review *Biotechnol. Adv.*, *19*, 35-63.
- 613 Cannon, P., St Pierre, L. E., & Miller, A. A. (1960). Solubilities of hydrogen and oxygen in polydimethylsiloxanes. *J.*  
614 *Chem. Eng. Data*, *5*, 236.
- 615 Césario, M. T., Baverloo, W. A., Tramper, J., & Beertink, H. H. (1997a). Enhancement of gas liquid mass transfer rate  
616 of apolar pollutants in the biological waste gas treatment by a dispersed organic solvent. *Enzyme Microb.*  
617 *Technol.*, *21*, 578-588.

- 618 Césario, M. T., Brandsma, J. B., Boon, M. A., Tramper, J., & Beftink, H. H. (1998). Ethene removal from gas by  
619 recycling a water-immiscible solvent through a packed absorber and a bioreactor. *J. Biotechnol.*, *62*, 105-118.
- 620 Césario, M. T., de Wit, H. L., Tramper, J., & Beftink, H. H. (1997b). Dispersed organic solvent to enhance the overall  
621 gas/water mass transfer coefficient of apolar compounds in the biological waste-gas treatment. Modeling and  
622 evaluation. *Biotechnol. Prog.*, *13*, 399-407.
- 623 Cha, J. M., Cha, W. S., & Lee, J. H. (1999). Removal of organo-sulphur odour compounds by *Thiobacillus novellus*  
624 SRM, sulphur-oxidizing microorganisms. *Process Biochem.*, *34*, 659-665.
- 625 Clarke, K. G., & Correia, L. D. C. (2008). Oxygen transfer in hydrocarbon-aqueous dispersion and its applicability to  
626 alkane bioprocess: A review. *Biochem. Eng. J.*, *39*, 405-429.
- 627 Collins, L. D., & Daugulis, A. J. (1997a). Biodegradation of phenol at high initial concentration in two-phase  
628 partitioning batch and fed batch bioreactors. *Biotechnol. Bioeng.*, *55*, 155-162.
- 629 Collins, L. D., & Daugulis, A. J. (1997b). Characterization and optimization of a two-phase partitioning bioreactor for  
630 the biodegradation of phenol. *Appl. Microbiol. Biotechnol.*, *48*, 18-22.
- 631 Collins, L. D., & Daugulis, A. J. (1999a). Benzene/Toluene/p-Xylene degradation. Part I: Solvent selection and toluene  
632 degradation in a two-phase partitioning bioreactor. *Appl. Microbiol. Biotechnol.*, *52*, 354-359.
- 633 Collins, L. D., & Daugulis, A. J. (1999b). Part II. Effect of substrate interactions and feeding strategies in  
634 toluene/benzene and toluene/p-xylene fermentations in a partitioning bioreactor. *Appl. Microbiol. Biotechnol.*,  
635 *52*, 360-365.
- 636 Collins, L. D., & Daugulis, A. J. (1999c). Simultaneous biodegradation of benzene, toluene and p-xylene in a two-phase  
637 partitioning bioreactor: concept demonstration and practical application. *Biotechnol. Prog.*, *15*, 74-80.
- 638 Cui, H., & Turn, S. Q. (2009). Adsorption/desorption of dimethylsulfide on activated carbon modified with iron  
639 chloride. *App. Cat. B-Environ.*, *88*, 25-31.
- 640 Darracq, G., Couvert, A., Couriol, C., Amrane, A., & Le Cloirec, P. (2009). Absorption and biodegradation of  
641 hydrophobic VOCs: determination of Henry's constants and biodegradation levels. *Water Sci. Technol.*, *59*,  
642 1315-1322.
- 643 Darracq, G., Couvert, A., Couriol, C., Amrane, A., & Le Cloirec, P. (2010a). Integrated process for hydrophobic VOC  
644 treatment - Solvent choice. *Can. J. Chem. Eng.*, *88*(4), 655-660.
- 645 Darracq, G., Couvert, A., Couriol, C., Amrane, A., & Le Cloirec, P. (2010b). Kinetics of toluene and sulfur compounds  
646 removal by means of an integrated process involving the coupling of absorption and biodegradation. *J. Chem.*  
647 *Technol. Biotechnol.*, *85*, 1156-1161.
- 648 Darracq, G., Couvert, A., Couriol, C., Amrane, A., Thomas, D., Dumont, E., et al. (2010c). Silicone oil: An effective  
649 absorbent for hydrophobic Volatile Organic Compounds (VOC) removal. *J. Chem. Technol. Biotechnol.*, *85*,  
650 309-313.
- 651 Darracq, G., Couvert, A., Couriol, C., Amrane, A., Thomas, D., Dumont, E., et al. (2012). Optimization of the volume  
652 fraction of the NAPL, silicon oil, and biodegradation kinetics of toluene and DMDS in a TPPB. *Int. Biodeter.*  
653 *Biodeg.*, *71*, 9-14.
- 654 Daugulis, A. J. (2001). Two-phase partitioning bioreactors: a new technology platform for destroying xenobiotics.  
655 *Trends Biotechnol.*, *19*, 457-462.
- 656 Daugulis, A. J., & Boudreau, N. G. (2003). Removal and destruction of high concentration of gaseous toluene in a two-  
657 phase partitioning bioreactor by *Alcaligenes xylosoxidans*. *Biotechnol. Lett.*, *25*, 1421-1424.
- 658 De Bont, J. A. M. (1998). Solvent-tolerant bacteria in biocatalysis. *Trends Biotechnol.*, *16*, 493-498.
- 659 De Guardia, A. (1994). *Epuración de gaz comportant des composés organo-soufrés. Etude d'un procédé physico-*  
660 *chimique*. Université de Rennes 1, ENSCR,
- 661 Desai, J. D., & Banat, I. M. (1997). Microbial production of surfactants and their commercial potential. *Microbiol. Mol.*  
662 *Biol. Rev.*, *61*, 47-64.
- 663 Deshusses, M. A. (1997). Biological waste air treatment in biofilters. *Curr. Opin. Biotechnol.*, *8*, 335-339.
- 664 Devos, M., Patte, F., Rouault, J., Laffort, P., & Van Gemert, L. J. (1990). *Standardized human olfactory thresholds:*  
665 *Oxford University Press, New York.*
- 666 Déziel, E., Commeau, Y., & Villemur, R. (1999). Two-liquid-phase bioreactors for enhanced degradation of  
667 hydrophobic/toxic compounds. *Biodegradation*, *10*, 219-233.
- 668 Docherty, K. M., Dixon, J. K., & Kulpar, J. C. F. (2007). Biodegradation of imidazolium and pyridinium ionic liquids  
669 by an activated sludge microbial community. *Biodegradation*, *18*, 481-493.
- 670 Docherty, K. M., & Kulpa, C. F. (2005). Toxicity and antimicrobial activity of imidazolium and pyridinium ionic  
671 liquids. *Green Chem.*, *7*, 185-189.
- 672 Dumont, E., Andrès, Y., & Le Cloirec, P. (2006). Mass transfer coefficients of styrene and oxygen into silicone oil  
673 emulsions in a bubble reactor. *Chem. Eng. Sci.*, *61*, 5612-5619.
- 674 Dumont, E., Darracq, G., Couvert, A., Couriol, C., Amrane, A., Thomas, D., et al. (2010). Determination of partition  
675 coefficients of three volatile organic compounds (dimethylsulphide, dimethyldisulphide and toluene) in  
676 water/silicone oil mixtures. *Chem. Eng. J.*, *162*, 927-934.

- 677 Dumont, E., Darracq, G., Couvert, A., Couriol, C., Amrane, A., Thomas, D., et al. (2011). VOC absorption in a  
678 countercurrent packed-bed column using water/silicone oil mixtures: Influence of silicone oil volume fraction.  
679 *Chem. Eng. J.*, *168*, 241-248.
- 680 Dumont, E., & Delmas, H. (2003). Mass transfer enhancement of gas absorption in oil-in-water systems: a review.  
681 *Chem. Eng. Process.*, *42*, 419-438.
- 682 Eaton, R. W., & Ribbons, D. W. (1982). Metabolism of Dibutylphthalate and Phthalate by *Micrococcus sp.* Strain 12B.  
683 *J. Bacteriol.*, *151*, 48-57.
- 684 Efroymson, R. A., & Alexander, M. (1991). Biodegradation by an Arthrobacter species of hydrocarbons partitioned into  
685 an organic solvent. *App. Environ. Microbiol.*, *57*, 1441-1447.
- 686 Eibes, G., Moreira, M. T., Feijo, G., Daugulis, A. J., & Lema, J. M. (2007). Operation of a two-phase partitioning  
687 bioreactor for the oxidation of anthracene by the enzyme manganese peroxidase. *Chemosphere*, *66*, 1744-1751.
- 688 Estévez, E., Veiga, M. C., & Kennes, C. (2005). Biofiltration of waste gases with the fungi *Exophiala oligosperma* and  
689 *Paecilomyces variotii*. *Appl. Microb. Biotechnol.*, *67*, 563-568.
- 690 Fall, R. R., Brown, J. L., & Schaeffer, T. L. (1979). Enzyme recruitment allows the biodegradation of recalcitrant  
691 branched hydrocarbons by *Pseudomonas citronellis*. *Appl. Environ. Microbiol.*, *38*(4), 715-722.
- 692 Fazaelipour, M. H., & Shojaosadati, S. A. (2002). The effect of silicone oil on biofiltration of hydrophobic compounds.  
693 *Environ. Prog.*, *21*, 221-224.
- 694 Fei, W. Y., & Bart, H. J. (2001). Predicting diffusivities in liquids by the group contribution method. *Chem. Eng.*  
695 *Process.*, *40*, 531-335.
- 696 Fewson, C. A. Factors affecting the degradation hazardous recalcitrant materials. In R. F. S. o. Engineers (Ed.), *Proc.*  
697 *Int. Symp. Environ. Biotechnol., Ostend, 1991* (Vol. 1, pp. 173-183)
- 698 Fritsche W., & Hofrichter M. (2005). Aerobic Degradation by Microorganisms. In R. G. Rehm H.J. (Ed.),  
699 *Biotechnology set, 2<sup>nd</sup> Ed - Part XIb: Environmental Processes II - II Microbiological Aspects* (pp. 144-167):  
700 Wiley.
- 701 Gardin, H., Lebeault, J. M., & Pauss, A. (1999). Biodegradation of xylene and butyl acetate using an aqueous-silicon oil  
702 two phase system. *Biodegradation*, *10*, 193-200.
- 703 Ghoshal, S., Ramaswami, A., & Luthy, R. G. (1996). Biodegradation of naphthalene from coal tar and  
704 heptamethylnonane in mixed batch system. *Environ. Sci. Technol.*, *30*, 1282-1291.
- 705 Guieysse, B., Cirne, M. D. D. T. G., & Mattiasson, B. (2001). Microbial degradation of phenanthrene and pyrene in a  
706 two-liquid-phase-partitioning bioreactor. *Appl. Microbiol. Biotechnol.*, *56*, 796-802.
- 707 Guieysse, B., Hort, C., Platel, V., Munoz, R., Ondarts, M., & Revah, S. (2008). Biological treatment of indoor air for  
708 VOC removal: Potential and challenges. *Biotechnol. Adv.*, *26*, 398-410.
- 709 Hamed, T. A., Bayraktar, E., Mehmetoglu, U., & Mehmetoglu, T. (2004). The biodegradation of benzene, toluene and  
710 phenol in a two-phase system. *Biochem. Eng. J.*, *19*, 137-146.
- 711 Hansen, K. C., Zhou, Z., Yaws, C. L., & Aminabhavi, T. M. (1993). Determination of Henry's law constants of  
712 organics in dilute aqueous solutions. *J. Chem. Eng. Data.*, *38*, 546-550.
- 713 Hartikainen, T., Martikainen, P. J., Olkkonen, M., & Ruuskanen, J. (2002). Peat biofilter in long-term experiments for  
714 removing odorous sulphur compounds. *Water Air Soil Pollut.*, *133*, 335-348.
- 715 Hayachi, S., Kobayashi, T., & Honda, H. (2003). Simple and Rapid Cell Growth Assay Using Tetrazolium Violet  
716 Coloring Method for Screening of Organic Solvent Tolerant Bacteria. *J. Biosc. Bioeng.*, *96*, 360-363.
- 717 Heipieper, H. J., Grit, N., Cornelissen, S., & Meinhradt, F. (2007). Solvent-tolerant bacteria for biotransformations in  
718 two-phase fermentation system. *Appl. Microbiol. Biotechnol.*, *74*, 961-973.
- 719 Hernández, M., Quijano, G., Muñoz, R., & Bordel, S. (2011). Modeling of VOC mass transfer in two-liquid phase  
720 stirred tank, biotrickling filter and airlift reactors. *Chem. Eng. J.*, *172*, 961-969.
- 721 Heymes, F. (2005). *Traitement d'air chargé en COV hydrophobes par un procédé hybride :Absorption-Pervaporation.*  
722 Université de Montpellier II,
- 723 Heymes, F., Demoustier, P. M., Charbit, F., Fanlo, J. L., & Moulin, P. (2006). A new efficient absorption liquid to treat  
724 exhaust air loaded with toluene. *Chem. Eng. J.*, *115*, 225-231.
- 725 Heymes, F., Demoustier, P. M., Charbit, F., Fanlo, J. L., & Moulin, P. (2007). Treatment of gas containing hydrophobic  
726 VOCs by a hybrid absorption-pervaporation process: the case of toluene. *Chem. Eng. Sci.*, *62*, 2576-2589.
- 727 Hine, J., & Weimar, J. R. D. (1965). Carbon Basicity. *J. Am. Chem. Soc.*, *87*, 3387-3396.
- 728 Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A., & Rogers, R. D. (2001).  
729 Characterization and comparaiso of hydrophilic and hydrophobic room temperature ionic liquids  
730 incorporating the imidazolium cation. *Green Chem.*, *3*, 156-164.
- 731 Iliuta, M. C., & Larachi, F. (2005a). Gas Liquid partition coefficients and Henry's law constants of DMS in aqueous  
732 solutions of Fe(II) chelate complexes using the static headspace method. *J. Chem. Eng. Data*, *50*, 1700-1705.
- 733 Iliuta, M. C., & Larachi, F. (2005b). Solubility of dimethyldisulfide (DMDS) in aqueous solutions of Fe(III) complexes  
734 of trans-1,2-cyclohexanediaminetetraacetic acid (CDTA) using the static headspace method. *Fluid phase*  
735 *Equilibria*, *233*, 184-189.
- 736 Inoue, A., & Horikoshi, K. (1991). Estimation of solvent-tolerance of bacteria by the solvent parameter log P. *J.*  
737 *ferment. Bioeng.*, *71*, 194-196.

- 738 Janikowski, T. B., Velicogna, D., Punt, M., & Daugulis, A. (2002). Use of a two-phase partitioning bioreactor for  
739 degrading polycyclic aromatic hydrocarbons by *Sphingomonas sp.*. *J. Appl. Microbiol. Biotechnol.*, *59*, 368-  
740 376.
- 741 Jimenez, I. Y., & Bartha, R. (1996). Solvent-Augmented Mineralization of Pyrene by a *Mycobacterium sp.* *App.*  
742 *Environ. Microbiol.*, *62*, 2311-2316.
- 743 Kennes, C., Rene, E. R., & Veiga, M. C. (2009). Bioprocess for air pollution control. *J. Chem. Technol. Biotechnol.*,  
744 *84*, 1419-1436.
- 745 Kester, A. S., & Foster, J. W. (1963). Diterminal oxidation of long chain alkanes by bacteria. *J. Bacteriol.*, *85*, 859-869.
- 746 Kirkwood, K. M., Chernik, P., Foght, J. M., & Gray, M. R. (2008). Aerobic biotransformation of decalin  
747 (decahydronaphtalene) by *Rhodococcus* spp. *Biodegradation*, *19*, 785-794.
- 748 Koma, D., Hasumi, F., Yamamoto, E., Ohta, T., Chung, S. Y., & Kumo, M. (2001). Biodegradation of long-chain n-  
749 paraffins from waste oil of car engine by *Acinetobacter sp.* *J. Biosci. Bioeng.*, *91*, 95-96.
- 750 Koma, D., Sakashita, Y., Kubota, K., Fujii, Y., Hasumi, F., Chung, S. Y., et al. (2003). Degradation of Car engine Base  
751 oil by *Rhodococcus sp.* NDKK48 and *Gordonia s.p.* NDKY76A. *Biosci. Biotechnol. Biochem.*, *67*, 1590-1593.
- 752 Laane, C., Boeren, S., & Vos, K. (1985). On optimizing organic solvents in multi-liquid-phase biocatalysis. *Trends*  
753 *Biotechnol.*, *3*, 251-252.
- 754 Laane, C., Boeren, S., Vos, K., & Veeger, C. (1987). Rules for optimization of biocatalysis in organic solvents.  
755 *Biotechnol. Bioeng.*, *30*, 81-87.
- 756 Le Cloirec, P. (1998). *Les composés organiques volatils (COV) dans l'environnement*. Paris: Lavoisier TEC&DOC.
- 757 Lee, E. H., & Cho, K. S. (2008). Characterization of cyclohexane and hexane degradation by *Rhodococcus sp.* EC1.  
758 *Chemosphere*, *71*, 1738-1744.
- 759 Liang, D. W., Zhang, T., Fang, H. H. P., & He, J. (2008). Phtalates biodegradation in the environment. *Appl. Microbiol.*  
760 *Biotechnol.*, *80*, 183-198.
- 761 Mackay, D., & Shiu, W. Y. (1981). A critical review of Henry's law constants for chemicals of environmental interest.  
762 *J. Phys. Chem. Ref. Data*, *10*, 1175-1199.
- 763 Mackay, D., Shiu, W. Y., & Sutherland, R. P. (1979). Determination of air-water Henry's law constants for  
764 hydrophobic pollutants. *Environ. Sci. Technol.*, *13*, 333-337.
- 765 MacLeod, C. T., & Daugulis, A. J. (2003). Biodegradation of polycyclic aromatic hydrocarbons in two phase  
766 partitioning bioreactor in the presence of a bioavailable solvent. *Appl. Microbiol. Biotechnol.*, *62*, 291-296.
- 767 MacLeod, C. T., & Daugulis, A. J. (2005). Interfacial effects in a two-phase partitioning bioreactor: degradation of  
768 polycyclic aromatic hydrocarbons (PAHs) by a hydrophobic *Mycobacterium*. *Process Biochem.*, *40*, 1799-  
769 1805.
- 770 MacMillan, J. D., & Wang, D. I. C. (1987). Enhanced oxygen transfer using oil-in-water dispersion. *Ann. NY Acad. Sci.*,  
771 *506*, 569-582.
- 772 Mahanty, B., Pakshirajan, K., & Venkata Dasu, V. (2010). A two liquid phase partitioning bioreactor system for the  
773 biodegradation of pyrene: Comparative evaluation and cost-benefit analysis. *J. Chem. Technol. Biotechnol.*,  
774 *85*(3), 349-355.
- 775 Mahanty, B., Parkshirajan, K., & Dasu, V. V. (2008). Biodegradation of pyrene by *Mycobacterium frederiksbergense* in  
776 a two-phase partitioning bioreactor system. *Bioresour. Technol.*, *99*, 2694-2698.
- 777 Malinowski, J. J. (2001). Two-phase partitioning bioreactors in fermentation technology. *Biotechnol. Adv.*, *19*, 525-538.
- 778 Marcoux, J., Déziel, E., Villemur, R., Lépine, F., Bisailon, J. G., & Beaudet, R. (2000). Optimization of high molecular  
779 weight polycyclic aromatic hydrocarbons' degradation in a two-liquid-phase bioreactor. *J. Appl. Microbiol.*,  
780 *88*, 655-662.
- 781 Matsumoto, M., Mochiduki, K., & Kondo, K. (2004). Toxicity of Ionic Liquids and Organic Solvents to Lactic Acid-  
782 Producing Bacteria. *J. Biosci. Bioeng.*, *98*, 344-347.
- 783 Miller, J. M., & Allen, D. G. (2004). Transport of hydrophobic pollutants through biofilms in biofilters. *Chem. Eng.*  
784 *Sci.*, *59*, 3515-3525.
- 785 Mohseni, M., & Allen, D. G. (2000). Biofiltration of hydrophilic and hydrophobic volatile organic compounds. *Chem.*  
786 *Eng. Sci.*, *55*, 1545-1558.
- 787 Montes, M., C. Veiga, M. C., & Kennes, C. (2011). Effect of oil concentration and residence time on the biodegradation  
788 of  $\alpha$ -pinene vapours in two-liquid phase suspended-growth bioreactors. *J. Biotechnol.*,  
789 doi:10.1016/j.jbiotec.2011.1007.1019.
- 790 Muñoz, R., Arriaga, S., Hernandez, S., Guieysse, B., & Revah, S. (2006). Enhanced hexane biodegradation in a two  
791 phase partitioning bioreactor: overcoming pollutant transport limitations. *Process Biochem.*, *41*, 1614-1619.
- 792 Muñoz, R., Villaverde, S., Guieysse, B., & Revah, S., T, (2007). Two-phase partitioning bioreactor for treatment of  
793 volatile organic compounds. *Biotechnol. Adv.*, *25*, 410-422.
- 794 Nakahara, T., Erickson, L. E., & Gutierrez, J. R. (1977). Characteristics of hydrocarbons uptake in cultures with two  
795 liquid phases. *Biotechnol. Bioeng.*, *19*, 9-25.
- 796 Nalli, S., Cooper, D. G., & Nicell, J. A. (2006). Metabolites from the biodegradation of di-ester plasticizers by  
797 *Rhodococcus rhodochrous*. *Sci. Total Environ.*, *366*, 286-294.

- 798 Nendza, M. (2007). Hazard assessment of silicone oils (polydimethylsiloxanes, PDMS) used in antifouling-/foul-  
799 release-products in the marine environment. *Mar. Pollut. Bull.*, *54*, 1190-1196.
- 800 Nhi-Cong, L. T., Mikolash, A., Klenk, H. P., & Schauer, F. (2009). Degradation of the multiple branched alkane  
801 2,6,10,14-tetramethyl-pentadecane (pristine in *Rhodococcus ruber* and *Mycobacterium neoaurum*). *Int.*  
802 *Biodeter. Biodegr.*, *63*, 201-207.
- 803 Nielsen, D. R., Daugulis, A. J., & Mclellan, P. J. (2005). Transient performance of a two-phase partitioning bioscrubber  
804 treating a benzene-contamination gas stream. *Environ. Sci. Technol.*, *39*, 8971-8977.
- 805 Ogino, H., Miyamoto, K., Yasuda, M., Ishimi, K., & Ishikawa, H. (1999). Growth of organic solvent-tolerant  
806 *Pseudomonas aeruginosa* LST-03 in the presence of various organic solvents and production of lipolytic  
807 enzyme in the presence of cyclohexane. *Biochem. Eng. J.*, *4*, 1-6.
- 808 Oliveira, F. J. S., & De França, F. P. (2005). Increase in removal of polycyclic aromatic hydrocarbons during  
809 bioremediation of crude oil-contaminated sandy soil. *Appl. Biochem. Biotechnol.*, *121-124*, 593-603.
- 810 Osborne, S. J., Leaver, J., Turner, M. K., & Dunill, P. (1990). Correlation of biocatalytic activity in an organic-aqueous  
811 two-liquid phase system with solvent concentration in the cell membrane. *Enzyme Microb. Technol.*, *12*, 281-  
812 291.
- 813 Osswald P., Baveye, P., & Block, J. C. (1996). Bacterial influence on partitioning rate during the biodegradation of  
814 styrene in a biphasic aqueous-organic system. *Biodegradation*, *7*, 297-302.
- 815 Ottengraf, S. P. P., Meesters, J. J. P., Van den Oever, A. H. C., & Rozema, H. R. (1986). Biological of volatile  
816 xenobiotics compounds in biofilters. *Bioproc. Biosyst. Eng.*, *1*, 61-69.
- 817 Pernafteta-Boldù, F. X., Illa, J., Van Groenestijn, J. W., & Flotats, X. (2008). Influence of the synthetic packing  
818 materials on the gas dispersion and biodegradation kinetics in fungal air biofilters. *Appl. Microbiol.*  
819 *Biotechnol.*, *79*, 319-327.
- 820 Poddar, T. K., Majumdar, S., & Sirkar, K. K. (1996). Removal VOCs from air by membrane based absorption and  
821 stripping. *J. Membr. Sci.*, *120*, 221-237.
- 822 Poddar, T. K., & Sirkar, K. K. (1996). Henry's constant for selected volatile organic compounds in high-boiling oils. *J.*  
823 *Chem. Eng. Data*, *41*, 1329-1332.
- 824 Quijano, G., Couvert, A., & Amrane, A. (2010a). Ionic liquids : Applications and future trends in bioreactor technology.  
825 *Bioresour. Technol.*, *101*, 8923-8930.
- 826 Quijano, G., Couvert, A., Amrane, A., Darracq, G., Couriol, C., Le Cloirec, P., et al. (2011a). Potential of ionic liquids  
827 for VOC absorption and biodegradation in multiphase systems. *Chem. Eng. Sci.*, *66*, 2707-2712.
- 828 Quijano, G., Couvert, A., Amrane, A., Darracq, G., Couriol, C., Le Cloirec, P., et al. (2011b). Toxicity and  
829 biodegradability of ionic liquids: New perspectives towards whole-cell biotechnological applications. *Chem.*  
830 *Eng. J.*, *174*, 27-32.
- 831 Quijano, G., Hernandez, M., Thalasso, F., Muñoz, R., & Villaverde, S. (2009). Two-phase partitioning bioreactor in  
832 environment biotechnology. *Appl. Microbiol. Technol.*, *84*, 829-846.
- 833 Quijano, G., Rocha-Ríos, J., Hernández, M., Villaverde, S., Revah, S., Muñoz, R., et al. (2010b). Determining the effect  
834 of solid and liquid vectors on the gaseous interfacial area and oxygen transfer rates in two-phase partitioning  
835 bioreactors. *J. Hazard. Mater.*, *175*, 1085-1089.
- 836 Rehmann, L., & Daugulis, A. J. (2007). Biodegradation of biphenyl in a solid-liquid two-phase partitioning bioreactor.  
837 *Biochem. Eng. J.*, *36*, 195-201.
- 838 Revah, S., & Morgan-Sagastume, J. M. (2005). .Methods of Odor and VOC Control. In S. A. Shareefdeen Z. (Ed.),  
839 *Biotechnology for Odour and Air Pollution Control* (pp. 29-63). Berlin Springer-Verlag, Berlin Heidelberg.
- 840 Robbins, G. A., Wang, S., & Stuart, J. D. (1993). Using the static headspace method to determine Henry's law constant.  
841 *Anal. Chem.*, *65*, 3113-3118.
- 842 Rodriguez, M., Klason, T. K., & Davison, B. H. (2001). Enhancement of the conversion of toluene by *Pseudomonas*  
843 *putida* F-1 using organic cosolvents. *Appl. Biochem. Biotechnol.*, *92-93*, 195-204.
- 844 Rols, J. L., Condoret, J. S., Fonade, C., & Goma, G. (1990). Mechanisms of enhanced oxygen transfer in fermentation  
845 using emulsified oxygen-vectors. *Biotechnol. Bioeng.*, *35*, 427-435.
- 846 Rontani J.F., Mouzdahir, A., Michotey, V., & Bonin, P. C. (2002). Aerobic and anaerobic metabolism of squalene by a  
847 denitrifying bacterium isolated from marine sediment. *Arch. Microbiol.*, *178*, 279-287.
- 848 Rontani, J. F., Bonin, P. C., & Volkman, J. K. (1999). Biodegradation of Free Phytol by Bacterial Communities Isolated  
849 from Marine Sediments under Aerobic and Denitrifying Conditions. *Appl. Environ. Microbiol.*, *65*, 5484-  
850 5492.
- 851 Rontani, J. F., & Giusti, G. (1986). Study of the biodegradation of poly-branched alkanes by a marine bacterial  
852 community. *Mar. Chem.*, *20*, 197-205.
- 853 Roustan., M. (2003). *Transfert gaz-liquide dans les procédés de traitement des eaux et des effluents gazeux*. Paris:  
854 Lavoisier TEC&DOC.
- 855 Sáez-Navarrete, C., Gelmi, C. A., Reyes-Bozo, L., & Godoy-Faúndez, A. (2008). An exploratory study of peat and  
856 sawdust as enhancers in the (bio)degradation on n-dodecane. *Biodegradation*, *19*, 527-534.
- 857 Sardesai, Y., & Bhosle, S. (2002). Tolerance of bacteria to organic solvents. *Res. Microbiol.*, *153*, 263-268.
- 858 Scheibel, E. G. (1954). Liquid diffusivities and viscosity of gases. *Ind. Eng. Chem.*, *46*, 2007-2008.

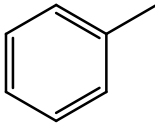
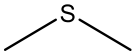
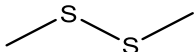
- 859 Seubert, W. (1960). Degradation of isoprenoid compounds by microorganisms. I. Isolation and characterization of an  
860 isoprenoid-degrading bacterium, *Pseudomonas citronellolis* n. sp. *J. Bacteriol.*, *79*, 426-434.
- 861 Shu, C. H., & Chen, C. K. (2009). Enhanced removal of dimethyl sulphide from a waste gas stream using a bioreactor  
862 inoculated with *Micobacterium* sp. NTUT26 and *Pseudomonas putida*. *J. Ind. Microbiol. Biotechnol.*, *36*, 95-  
863 104.
- 864 Sikkema, J., de Bont, J. A., & Poolman, B. (1995). Mechanisms of membrane toxicity of hydrocarbons. *Microbiol.*  
865 *Rev.*, *59*, 201-222.
- 866 Singh, A., Shareefdeen, Z., & Ward, O. P. (2005). Biotechnology for Odour and Air pollution control. In *Bioscrubber*  
867 *Technology*. Berlin Springer-Verlag, Berlin Heidelberg.
- 868 Singh, D., & Fulekar, M. H. (2010). Benzene bioremediation using cow dung microflora in two phase partitioning  
869 bioreactor. *J. Hazard. Mater.*, *175*, 336-343.
- 870 Singh, L., Ram, M. S., Agarwal, M. K., & Alam, S. I. (2000). Characterization of *Aeromonas hydrophila* strains and  
871 their evaluation for biodegradation of night soil. *J. Microbiol. Biotechnol.*, *16*, 625-630.
- 872 Solano-Serena, F., Marchal, R., Heiss, S., & Vandecasteele, J. P. (2004). Degradation of isooctane by *Mycobacterium*  
873 *austrorfricanum* IFP 2173: growth and catabolic pathway. *J. Appl. Microbiol.*, *97*, 629-639.
- 874 Staudinger, J., & Roberts, P. V. (2000). A critical compilation of Henry's law constant temperature dependence  
875 relations for organic compounds in dilute aqueous solutions. *Chemosphere*, *44*, 561-576.
- 876 Tomei, M. C., Annesini, R. S., & Daugulis, A. J. (2008). Biodegradation of 4-nitrophenol in a two-phase sequencing  
877 batch reactor : concept demonstration, kinetics and modelling. *Appl. Microbiol. Biotechnol.*, *80*, 1105-1112.
- 878 Trinci, A. P. J. (1969). A kinetic study of the growth of *Aspergillus nidulans* and other fungi. *J. Gen. Microbiol.*, *57*, 11-  
879 24.
- 880 Tudose, R. Z., & Apreotesei, G. (2001). Mass transfer coefficients in liquid-liquid extraction. *Chem. Eng. Process.*, *40*,  
881 447-485.
- 882 Van der Meer, J. R., de Vos, W. M., Harayama, S., & Zehnder, A. J. B. (1992). Molecular mechanisms of genetic  
883 adaptation to xenobiotic compounds. *Microbiol. Rev.*, *56*, 677-694.
- 884 Van der Werf, M. J., Swarts, H. J., & de Bont, J. A. M. (1999). *Rhodococcus erythropolis* DCL14 contains a novel  
885 degradation pathway for limonene. *Appl. Environ. Microbiol.*, *65*, 2092-2102.
- 886 Vannek, P., Beekman, M., de Saeyer, N., D'Haene, S., & Verstraete, W. (1995). Biodegradation of polycyclic aromatic  
887 hydrocarbons in a two-liquid phase system. In R. R. Hinchee, D. B. Anderson, & R. E. Hoepfel (Eds.),  
888 *Bioremediation of Recalcitrant Organics* (Vol. 7, pp. 55-62): Batelle Press.
- 889 Vieira, P. A., Vieira, R. B., de Franc, F. P., & Cardoso, V. L. (2007). Biodegradation of effluent contaminated with  
890 diesel fuel and gasoline. *J. Hazard. Mater.*, *140*, 52-59.
- 891 Vrionis, H. A., Kropinski, A. M., & Daugulis, A. J. (2002). Enhancement of a Two-Phase Partitioning bioreactor  
892 system by modification of the microbial catalyst: Demonstration of concept. *Biotechnol. Bioeng.*, *79*, 587-594.
- 893 Vuong, M. D., Couvert, A., Couriol, C., Amrane, A., Le Cloirec, P., & Renner, C. (2009). Determination of the Henry's  
894 constant and the mass transfer rate of VOCs in solvents. *Chem. Eng. J.*, *150*, 426-443.
- 895 Welton, T. (1999). Room-Temperature Ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.*, *99*, 2071-2084.
- 896 Wilke, C. R., & Chang, P. (1955). Correlation of diffusion coefficients in dilute solutions. *AIChE J.*, *1*, 264-270.
- 897 Woodley, J. M., Brazier, A. J., & Lilly, M. G. (1991). Lewis cell studies to determine reactor design data for two-liquid-  
898 phase bacterial and enzymatic reactions. *Biotechnol. Bioeng.*, *37*, 133-140.
- 899 Xia, B., Majumbar, S., & Sirkar, K. K. (1999). Regenerative oil scrubbing of volatile organic compounds from a gas  
900 stream in hollow fiber membrane devices. *Ind. Eng. Chem. Res.*, *38*, 3462-3472.
- 901 Yang, Z., & Pan, W. (2005). Ionic liquids: Green solvents for non aqueous biocatalysis. *Enzyme Microb. Technol.*, *37*,  
902 19-28.
- 903 Yeom, S. H., & Daugulis, A. J. (2000). Treatment of high concentration gaseous benzene stream using a novel  
904 bioreactor system. *Biotechnol. Lett.*, *22*, 1747-1751.
- 905 Yeom, S. H., & Daugulis, A. J. (2001a). Development of a novel bioreactor system for treatment of gaseous benzene.  
906 *Biotechnol. Bioeng.*, *72*, 156-165.
- 907 Yeom, S. H., & Daugulis, A. J. (2001b). A two-phase partitioning bioreactor system for treating benzene-contaminated  
908 soil. *Biotechnol. Lett.*, *23*, 467-473.
- 909 Zhang, F., Ni, Y., Sun, Z., Zheng, P., Lin, W., Zhu, P., et al. (2008). Asymmetric Reduction of Ethyl 4-Chloro-3-  
910 oxobutanoate to Ethyl(S)-4-Chloro-3-hydroxybutanoate catalyzed by *Aureobasidium pullulans* in an  
911 aqueous/Ionic liquid biphasic System. *Chin. J. Catal.*, *29*, 577-582.
- 912 Zhang, Y., Liss, S. N., & Allen, D. G. (2007). Enhancing and modelling the biofiltration of dimethyl sulphide under  
913 dynamic methanol addition. *Chem. Eng. Sci.*, *62*, 2474-2781.
- 914 Zhao, D., Liao, Y., & Zhang, Z. (2007). Toxicity of ionic liquids. *Clean*, *35*, 42-48.
- 915
- 916
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918 **Figure captions**919 **Figure 1.** Procedure for the choice of the process to be implemented for loaded VOC air treatment (Smeets,  
920 2002)921 **Figure 2.** Hybrid absorption-biodegradation process with regeneration of the organic phase922 **Figure 3.** Mass transfer phenomena in a two-phase partitioning bioreactor923 **Figure 4.** Structure of silicone oils (a), polydimethylsiloxane (PDMS) and polymethylphenylsiloxane (PMPS),  
924 as well as that of ionic liquids (b) with various

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926

927 **Table 1.** Physical and chemical properties of toluene, DMS and DMDS (Cui and Turn 2009; Staudinger and  
928 Roberts 2000; Muñoz et al. 2007)

Compounds	Toluene	DMS	DMDS
<b>Properties</b>			
<b>CAS number</b>	108-88-3	75-18-3	624-92-0
<b>Formula</b>			
	$C_6H_5-CH_3$	$(CH_3)_2S$	$(CH_3)_2S_2$
<b>Molar weight (g.mol<sup>-1</sup>)</b>	92.1	62.1	94.2
<b>Density</b>	0.867	0.840	1.063
<b>Boiling point (°C)</b>	110.6	37.3	109.8
<b>Vapour pressure (atm)</b>	0.029 (20°C)	0.660 (25°C)	0.038 (25°C)
<b>Partition coefficient octanol/water : log K<sub>ow</sub></b>	2.6	0.9	1.8
<b>Solubility in water (mg.L<sup>-1</sup>)</b>	526 (25°C)	20.5 (20°C)	2.5 (20°C)
<b>Henry's constant in water (atm.m<sup>3</sup>.mol<sup>-1</sup>)</b>	$6.4 \cdot 10^{-3}$ (25°C)	$1.61 \cdot 10^{-3}$ (25°C)	$1.21 \cdot 10^{-3}$ (20°C)
<b>Olfactory threshold (µg.m<sup>-3</sup>)</b>	8200	1.50	0.10 (8 to 10 ppb)
<b>Odour</b>	Plastic <sup>a</sup>	Vegetable in decomposition	Putrid

929 <sup>a</sup>Devos et al. (Devos et al. 1990)



**Table 2.** Examples of multiphase bioreactor systems

Family compounds	Xenobiotic or hydrophobic substrate	Microorganisms	Non-aqueous phase liquid	References
Hydrocarbons BTEX	Toluene	<i>Pseudomonas</i> sp., <i>Alcaligenes xylooxidans</i> , mixed culture	Oleyl alcohol, hexadecane, DEHA*	(Collins and Daugulis 1999a, 1999b, 1999c; Daugulis and Boudreau 2003; Darracq et al. 2009)
	Benzene	<i>Klebsiella</i> sp. <i>Achromobacter xylooxidans</i> <i>Pseudomonas putida</i>	Octadecene Hexadecane n-Hexadecane	(Yeom and Daugulis 2001b) (Nielsen et al. 2005)
	Xylene	<i>Pseudomonas</i> sp.	Oleyl alcohol	(D. Singh and Fulekar 2010) (Collins and Daugulis 1999b)
PAH*	Pyrene	<i>Mycobacterium frederiksbergense</i>	Silicone oil	(Mahanty et al. 2008; Mahanty et al. 2010)
	Various PAHs	<i>Mycobacterium</i> <i>Sphingomonas</i> sp.	Bis(ethylhexyl)sebacate Dodecane	(MacLeod and Daugulis 2005)
	Naphtalene, Phenanthrene	<i>Pseudomonas</i> sp., <i>Bacillus</i> <i>Pseudomonas</i> sp. Mixed culture	Decane, Octadecane, hexane Silicon oil, HMN	(Janikowski et al. 2002) (Abe et al. 1995)
	Various PAHs	Bacteria consortium	Hexadecane, dibutylphtalate Silicone oil, Paraffin oil, HMN*	(Bouchez et al. 1995) (Birman and Alexander 1996) (Marcoux et al. 2000; Vannek et al. 1995)
Alkanes, Alkenes	Hexane, Styrene, Ethene $\alpha$ -pinene	<i>Pseudomonas aeruginosa</i> Mixed culture <i>Micobacterium parafortuitum</i> Mixed culture	Silicone oil Silicone oil Fluorocarbon 40 Silicone oil	(Muñoz et al. 2006) (Osswald P. et al. 1996) (Césario et al. 1998) (Montes et al. 2011)
	Sulphur compounds	DMS, DMDS	Mixed culture	DEHA (Darracq et al. 2009, 2010b)
Chlorinated compounds	2,4,6-trichlorophenol	<i>Pseudomonas</i> sp.	Silicone oil	(Ascon-Cabrera and Lebeault 1995)
	1,2-dichlorobenzene	Mixed culture		
	1,2,3-trichlorobenzene	Mixed culture	Silicone oil	
	1,2,4-trichlorobenzene	Mixed culture		(Ascon-Cabrera and

Other molecules	Phenol Decahydronaphtalene 4-nitrophenol	<i>Pseudomonas putida</i> <i>Rhodococcus</i> spp. Mixed culture	2-undecanone HMN Undecanol, 2-undecanone, oleyl alcohol	Lebeault 1993) (Collins and Daugulis 1997a, 1997b) (Kirkwood et al. 2008) (Tomei et al. 2008)
	Ethyl butyrate, 2- Ethylbutyraldehyde, Butyraldehyde	Mixed culture	Silicone oil	(Ascon-Cabrera and Lebeault 1993)

DEHA: Di(2-EthylHexyl)Adipate, PAH: Polycyclic Aromatic Hydrocarbons, HMN: HeptaMethylNonane, DMS: DiMethylSulphide, DMDS: diMethylDiSulphide

**Table 3.** Comparison between different biological treatments and the alternative process (Mohseni and Allen 2000; Burgess et al. 2001; Miller and Allen 2004; A. Singh et al. 2005; Muñoz et al. 2007; Deshusses 1997; Kennes et al. 2009)

Characteristics	Biofilter	Biotrickling filter	Bioscrubber	The Considered process Absorber + TPPB
<b>Design</b>	One reactor (open)	One reactor (closed)	Two reactors	Two reactors
<b>Liquid absorbent</b>	Water	Water	Water	NAPL
<b>Solid phase for absorption</b>	Natural filter bed or inert	Exclusively inert packing materials	Inert packing materials	Inert packing materials
<b>Composition of liquid</b>	Water with microorganisms and nutrients	Water	Water	Organic Solvent or emulsion water/NAPL
<b>Surface area</b>	High	Low	Low	Low
<b>Concentration of pollutants and example</b>	< 1 g.m <sup>-3</sup> Toluene, DMS, Styrene, $\alpha$ -pinene, H <sub>2</sub> S, Methanol	< 0.5 g.m <sup>-3</sup> Ethanol, Ammonia, DMS, H <sub>2</sub> S, Phenol, Trichloroethylene	< 5 g.m <sup>-3</sup> H <sub>2</sub> S, SO <sub>2</sub> , Alcohols, aldehydes, Amines, Odours	< 0.1 g.m <sup>-3</sup> Hexane, Toluene, Dichloromethane, styrene
<b>Suitable for compounds with Henry's constant in water (Pa.m<sup>3</sup>.mol<sup>-1</sup>)</b>	< 1	< 0.1	< 0.01	> 1 in water
<b>Biomass</b>	Fixed	Fixed	Suspension	Suspension
<b>Clogging of packing</b>	Problem	Problem	No problem	No problem
<b>Advantages</b>	Suitable for hydrophobic and poorly water compounds removal  Microorganisms naturally present in the medium  Various types of microorganisms (bacteria, fungi, etc)	An easy control of the operating conditions owing to the presence of a mobile liquid phase  Inert packing materials allows to increase the gas/liquid transfer	Two-step process, packed column and bioreactor, recalcitrant pollutants removed in the bioreactor  An easy control of the operating conditions owing to the presence of a mobile liquid phase  Activated sludge units commonly used	Removal of poorly water soluble compounds and hydrophobic pollutants  High pollutant concentrations in NAPL, so microorganisms are not exposed to high concentrations in water  High L/G ratio but NAPL is regenerated  Enhanced absorber performances with NAPL as

absorbent

High interfacial area in  
bioreactor by surfactant  
addition

**Drawbacks**

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Medium acidification			
Media degradation, high built-up area, high pressure drop increase and low removal efficiency	High L/G ratio, so operation cost increase and biofilm detachment		Pollutants degraded in the aqueous phase
Compulsory humidification of the gas effluent	Higher residence time in reactor for recalcitrant compounds than for readily biodegradable pollutants	Low residence time in packed column which does not allow hydrophobic VOC absorption	Difficult to find a NAPL non biodegradable and easy to regenerate
Biodegradation increases medium temperature	Biomass accumulation leading to pressure drop increase	Biomass accumulation, so increase of pressure drop but the high liquid flow rates minimise growth in the scrubber	Viscous NAPL increase the pressure drop in the absorber
Specific inoculums required to treat recalcitrant compounds	Non-homogenous biomass distribution		High stirring energy for aeration and agitation
Absorption/desorption cycles			
Operating conditions (pH, Humidity, water activity, temperature, etc)			
Risk of anaerobic zones			

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**Table 4.** Henry's constants of hydrophobic VOC in water

VOC	H (Pa.m <sup>3</sup> .mol <sup>-1</sup> )	T (K)	References
Toluene	675	298	(Mackay et al. 1979)
	670	298	(Mackay and Shiu 1981)
	652	298	(Robbins et al. 1993)
	615	298	(Dumont et al. 2010)
	722	301	(Hansen et al. 1993)
	515	295	(Césario et al. 1997b)
	509	293	(Staudinger and Roberts 2000)
Dimethylsulphide	124	298	(Dumont et al. 2010)
	180	293	(Hine and Weimar 1965)
	155	293	(Staudinger and Roberts 2000)
	118	288	(Iliuta and Larachi 2005a)
	124	298	(Darracq et al. 2010c)
Dimethyldisulphide	122	298	(Dumont et al. 2010)
	111	293	(Hine and Weimar 1965)
	77	293	(Staudinger and Roberts 2000)
	112	298	(Iliuta and Larachi 2005b)
	119	298	(Darracq et al. 2010c)
Benzene	562	298	(Mackay et al. 1979)
	535	298	(Robbins et al. 1993)
	649	302	(Hansen et al. 1993)
	466	293	(Staudinger and Roberts 2000)
p-Xylene	710	298	(Mackay and Shiu 1981)
	856	300	(Hansen et al. 1993)
o-Xylene	604	293	(Staudinger and Roberts 2000)
	500	298	(Mackay and Shiu 1981)
m-Xylene	390	293	(Staudinger and Roberts 2000)
	700	298	(Mackay and Shiu 1981)
	561	293	(Staudinger and Roberts 2000)
Ethylbenzene	854	298	(Mackay et al. 1979)
	583	293	(Staudinger and Roberts 2000)

**Table 5.** Henry's constants of hydrophobic VOC (Toluene, DMS and DMDS) in organic NAPL ( $\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ ) or water/NAPL emulsions

NAPL (viscosity)	VOC		
	Toluene	DMS	DMDS
DEHA (12.5 mPa.s)	0.9 (25°C) (Vuong et al. 2009) 0.7 (25°C) (F. Heymes 2005)	19.5 (25°C) (Vuong et al. 2009)	1.1 (25°C) (Vuong et al. 2009)
DIB* Phtalate (37.8 mPa.s)	0.9 (25°C) (F. Heymes 2005)	-	-
DIH* Phtalate (55.0 mPa.s)	1.0 (25°C) (F. Heymes 2005)	-	-
DID* Phtalate (118.8 mPa.s)	1.1 (25°C) (F. Heymes 2005)	-	-
DEH Phtalate	0.2 (18°C) (Bourgois et al. 2006)	-	-
Silicone oil (3 mPa.s)	-	8.1 (25°C) (De Guardia 1994)	2.1 (25°C) (De Guardia 1994)
Silicone oil (5 mPa.s)	2.3 (25°C) (Dumont et al. 2011)	17.7 (25°C) (Dumont et al. 2011)	3.4 (25°C) (Dumont et al. 2011)
Silicone oil (20 mPa.s)	1.8 (25°C) (F. Heymes 2005)	-	-
Silicone oil (50 mPa.s)	6.9 (25°C) (Poddar et al. 1996)	-	-
Silicone oil (50 mPa.s)	12.1 (45°C) (Xia et al. 1999)	-	-
Silicone oil (500 mPa.s)	7.1 (25,6°C) (Poddar and Sirkar 1996)	-	-
PEG 300	2.16 (25°C) (F. Heymes 2005)	-	-
PEG 400	1.41 (25°C) (F. Heymes 2005)	-	-
PEG 400	1.51 (25°C) (Vuong et al. 2009)	22.9 (25°C) (Vuong et al. 2009)	1.8 (25°C) (Vuong et al. 2009)
Paratherm oil (30 mPa.s)	14.3 (30°C) (Poddar and Sirkar 1996)	-	-
n-Hexadecane	2.5 (25°C) (Vuong et al. 2009)	21.7 (25°C) (Vuong et al. 2009)	1.7 (25°C) (Vuong et al. 2009)
Oleyl alcohol	1.5 (25°C) (Vuong et al. 2009)	1.9 (25°C) (Vuong et al. 2009)	6.9 (25°C) (Vuong et al. 2009)
Perfluorocarbon FC40	29.4 (22°C) (Césario et al. 1997b)	-	-
FC40/water	-	-	-
1%v/v FC40	417 (22°C) (Césario et al. 1997a)	-	-
3%v/v FC40	319 (22°C) (Césario et al. 1997a)	-	-
5%v/v FC40	245 (22°C) (Césario et al. 1997a)	-	-
10%v/v FC40	186 (22°C) (Césario et al. 1997a)	-	-

\*Di-2-EthylHexylPhthalate (DEHP), Di-Iso-HeptylPhthalate (DIHP) and Di-Iso-NonylPhthalate (DINP)

**Table 6.** Global mass transfer coefficient  $K_L a$  ( $s^{-1}$ ) in gas-liquid contactors containing various liquid absorbents

Solvents	VOC			References
	Toluene	DMS	DMDS	
Water	[7.8-8.3] $10^{-3}$ 1.4 $10^{-3}$ 1.8 $10^{-2}$	4.0 $10^{-3}$	1.8 $10^{-3}$	(F. Heymes et al. 2007) (Darracq et al. 2010c) (Césario et al. 1997a)
DEHA	2.5 $10^{-4}$ 2.51 $10^{-4}$ to 2.43 $10^{-3}$	4.68 $10^{-4}$	1.04 $10^{-4}$	(Vuong et al. 2009) (F. Heymes et al. 2007)
DiEthylHexylPhtalate Cables-bundle Pall metal ring	[2.33-3.28] $10^{-4}$ 3.1 $10^{-4}$	-	-	(Bourgois et al. 2009)
Silicone oil (5 mPa.s)	1.6 $10^{-3}$	4.0 $10^{-3}$	1.6 $10^{-3}$	(Darracq et al. 2010c)
PEG 400	[1.4-5.5] $10^{-4}$	-	-	(F. Heymes et al. 2007)
1 to 10% vv of FC40 in water	[1.6-2.0] $10^{-2}$	-	-	(Césario et al. 1997a)
Silicone oil (53 mPa.s)/water 10%v/v 30%v/v 50%v/v	1.6 $10^{-4}$ 3.3 $10^{-4}$ 1.6 $10^{-4}$	-	-	(Rodriguez et al. 2001)

**Table 7.** VOC diffusion coefficients  $D_L$  ( $\text{m}^2 \cdot \text{s}^{-1}$ ) in various liquid absorbents

Solvents (viscosity)	VOC			References
	Toluene	DMS	DMDS	
Water (1 mPa.s)	$8.2 \cdot 10^{-10}(22^\circ\text{C})^a$	-	-	(Césario et al. 1997b)
DEHA (12.5 mPa.s)	$8.65 \cdot 10^{-10}(25^\circ\text{C})$	-	-	(F. Heymes et al. 2007)
DIH Phtalate <sup>b</sup> (46 mPa.s)	$7.43 \cdot 10^{-11}(20^\circ\text{C})$			
DEH Phtalate <sup>b</sup> (77 mPa.s)	$5.51 \cdot 10^{-11}(20^\circ\text{C})$	-	-	(Bourgois et al. 2009)
DIN Phtalate <sup>b</sup> (96 mPa.s)	$5.60 \cdot 10^{-11}(20^\circ\text{C})$			
DIB Phtalate (37.8 mPa.s)	$2.86 \cdot 10^{-11}(25^\circ\text{C})$			
DIH Phtalate (55.0 mPa.s)	$1.97 \cdot 10^{-10}(25^\circ\text{C})$	-	-	(F Heymes et al. 2006)
DID Phtalate (118.8 mPa.s)	$0.91 \cdot 10^{-10}(25^\circ\text{C})$			
Silicone oil (5 mPa.s)	$5.65 \cdot 10^{-11}(25^\circ\text{C})$	$5.13 \cdot 10^{-11}(25^\circ\text{C})$	$8.72 \cdot 10^{-12}(25^\circ\text{C})$	(Darracq et al. 2010c)
Silicone oil (20 mPa.s)	$5.46 \cdot 10^{-10}(25^\circ\text{C})$	-	-	(F Heymes et al. 2006)
Silicone oil (50 mPa.s)	$7.63 \cdot 10^{-10}(26^\circ\text{C})$	-	-	(Poddar et al. 1996)
Silicone oil (50 mPa.s)	$2.67 \cdot 10^{-10}(25^\circ\text{C})$	-	-	(Xia et al. 1999)
PEG 300	$0.81 \cdot 10^{-10}(25^\circ\text{C})$	-	-	
PEG 400	$1.43 \cdot 10^{-10}(25^\circ\text{C})$	-	-	(F Heymes et al. 2006)
Paratherm oil (30 mPa.s)	$4.80 \cdot 10^{-10}(25^\circ\text{C})$	-	-	(Poddar et al. 1996)
Perfluorocarbon FC40 (4.5 mPa.s)	$7.2 \cdot 10^{-10}(22^\circ\text{C})^a$	-	-	(Césario et al. 1997b)

<sup>a</sup>Estimated according to Wilke and Chang (Wilke and Chang 1955)

<sup>b</sup>di Di-2-EthylHexylPhthalate (DEHP), Di-Iso-HeptylPhthalate (DIHP) and Di-Iso-NonylPhthalate (DINP)



**Table 8.** Elimination capacity (EC) of toluene in Two-Phase Partitioning Bioreactor (TPPB)

NAPL/water ratio (%v/v)	Microorganisms	EC (g.m <sup>-3</sup> .h <sup>-1</sup> )	References
33% Oleyl alcohol	<i>Pseudomonas</i> sp.,	79	(Collins and Daugulis 1999c)
33% n-Hexadecane	<i>Alcaligenes xylooxidans</i>	733	(Daugulis and Boudreau 2003)
	<i>Achromobacter xylooxidans</i>	>326	(Boudreau and Daugulis 2006)
6% 2-Undecanone	<i>Pseudomonas putida</i>	197	(Hamed et al. 2004)
100% water	Mixed culture aquifer	0.96	(Alvarez and Vogel 1991)
	<i>Pseudomonas</i> sp. CFS-215	2.0	

**Table 9.** Physicochemical properties of various NAPL extensively used in Two-phase Partitioning Bioreactor (TPPB)

Name	Formula	Log Kow	Viscosity (Pa.s)	Superficial tension (N/m)	Solubility in water (g.L <sup>-1</sup> )	Biodegradability <sup>a</sup>
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	3.2 à 3.44	9.66 10 <sup>-4</sup>	2.53 10 <sup>-2</sup>	0.058	+ (Lee and Cho 2008 )
Hexane	C <sub>6</sub> H <sub>14</sub>	3.29	3.10 10 <sup>-4</sup>	1.85 10 <sup>-2</sup>	0.013	+ (Lee and Cho 2008 )
Ethylene glycol diehyl ether	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	0.77	7.27 10 <sup>-4</sup>	2.43 10 <sup>-2</sup>	20.4% en volume	+
Cyclooctene	C <sub>8</sub> H <sub>14</sub>	3.79	1.66 10 <sup>-3</sup>	2.94 10 <sup>-2</sup>	-	+ (Collins and Daugulis 1999a)
Isooctane	C <sub>8</sub> H <sub>18</sub>	4.09	5.07 10 <sup>-4</sup>	1.88 10 <sup>-2</sup>	Insoluble	+ (Solano-Serena et al. 2004)
Ethyl heptanoate	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	3.4	-	2.78 10 <sup>-2</sup>	0.29	+
(+)-Limonene	C <sub>10</sub> H <sub>16</sub>	4.1 à 4.83	-	-	1.38 10 <sup>-2</sup>	+ (Janikowski et al. 2002; Van der Werf et al. 1999)
1-Decyne	C <sub>10</sub> H <sub>18</sub>	4.67	1.32 10 <sup>-3</sup>	2.62 10 <sup>-2</sup>	-	+
Decene	C <sub>10</sub> H <sub>20</sub>	5.19	8.20 10 <sup>-4</sup>	2.48 10 <sup>-2</sup>	1.48 10 <sup>-4</sup>	+ (Vieira et al. 2007)
2,6-dimethyl-2-octene	C <sub>10</sub> H <sub>20</sub>	5.02	-	-	-	+ (Fall et al. 1979)
2-Decanone	C <sub>10</sub> H <sub>20</sub> O	3.2 to 3.7	-	-	7.68 10 <sup>-2</sup>	+ (Collins and Daugulis 1999a)
Décane	C <sub>10</sub> H <sub>22</sub>	5.25	9.30 10 <sup>-4</sup>	2.39 10 <sup>-2</sup>	-	+ (Fritsche W. and Hofrichter M. 2005; Kester and Foster 1963)
3,6-dimethyloctane	C <sub>10</sub> H <sub>22</sub>	5.1 to 5.9	-	-	-	+ (Fall et al. 1979)
1-decanol	C <sub>10</sub> H <sub>22</sub> O	3.8 to 4.6	1.39 10 <sup>-2</sup>	2.88 10 <sup>-2</sup>	Insoluble	+ (Kester and Foster 1963)
Dipentyl ether	C <sub>10</sub> H <sub>22</sub> O	3.96	1.08 10 <sup>-3</sup>	2.48 10 <sup>-2</sup>	Insoluble	+
2-Decanol	C <sub>10</sub> H <sub>22</sub> O	3.9	-	-	-	+ (Collins and Daugulis 1999a)
Jasmone	C <sub>11</sub> H <sub>16</sub> O	3.55 to 4.1	-	-	0.168	+ (Collins and Daugulis 1999a)
2-Undecanone	C <sub>11</sub> H <sub>22</sub> O	3.69 à 4.09	-	-	1.97 10 <sup>-2</sup>	+ (Fritsche W. and Hofrichter M. 2005)
Undecane	C <sub>11</sub> H <sub>24</sub>	5.74	1.20 10 <sup>-3</sup>	2.47 10 <sup>-2</sup>	Insoluble	+ (Kester and Foster 1963)
2-dodecanone	C <sub>12</sub> H <sub>24</sub> O	4.4	-	-	-	+ (Collins and Daugulis 1999a)
Dodecanal	C <sub>12</sub> H <sub>24</sub> O	4.7	2.04 10 <sup>-3</sup>	2.94 10 <sup>-2</sup>	Insoluble	+ (Fritsche W. and Hofrichter M. 2005)
Dodecane	C <sub>12</sub> H <sub>26</sub>	6.23	1.15 10 <sup>-3</sup>	2.54 10 <sup>-2</sup>	Insoluble (3.66 10 <sup>-6</sup> )	+ (Sáez-Navarrete et al. 2008)
Diethylsebacate	C <sub>14</sub> H <sub>26</sub> O <sub>4</sub>	4.33	-	-	0.08	+ (Nalli et al. 2006; Barnabe et al. 2008)

Tetradecane	C <sub>14</sub> H <sub>30</sub>	7.2	2.34 10 <sup>-3</sup>	2.66 10 <sup>-2</sup>	Insoluble	+ (Kester and Foster 1963)
Farnesol	C <sub>15</sub> H <sub>26</sub> O	5.4	-	-	Insoluble	+ (Berekaa and Steinbüch 2000; Seubert 1960)
Dibutylphthalate	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	4.5 à 4.7	2.13 10 <sup>-2</sup>	3.32 10 <sup>-2</sup>	0.13	+ (Eaton and Ribbons 1982)
Ethyl Myristate	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	6.9	-	-	Insoluble	+
HMN or 2,2,4,4,6,8,8-heptamethylnonane	C <sub>16</sub> H <sub>34</sub>	7.79	3.76 10 <sup>-3</sup>	2.53 10 <sup>-2</sup>	-	+ (Rontani and Giusti 1986)
n-Hexadecane	C <sub>16</sub> H <sub>34</sub>	8.2	1.18 10 <sup>-4</sup>	2.76 10 <sup>-2</sup>	Insoluble	+ (Fritsche W. and Hofrichter M. 2005; Muñoz et al. 2006)
Isopryl myristate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	7.17	5.60 10 <sup>-3</sup>	2.80 10 <sup>-2</sup>	Insoluble	+ (MacLeod and Daugulis 2003)
Linoleic Acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	7.3 à 7.5	2.31 10 <sup>-2</sup>	3.26 10 <sup>-2</sup>	Insoluble	+ (Kester and Foster 1963)
Octadecane	C <sub>18</sub> H <sub>34</sub>	9.18	3.87 10 <sup>-3</sup> at 29°C	2.77 10 <sup>-2</sup>	Insoluble	+ (Fritsche W. and Hofrichter M. 2005)
1-Octadecene	C <sub>18</sub> H <sub>36</sub>	9.04	4.31 10 <sup>-3</sup>	2.85 10 <sup>-2</sup>	Insoluble	+
Olehyll alcohol	C <sub>18</sub> H <sub>36</sub> O	7.5	-	-	Insoluble	+ (Fritsche W. and Hofrichter M. 2005)
Trihexylamine	C <sub>18</sub> H <sub>39</sub> N	7.4 à 7.8	-	-	Insoluble	-
Tridecylcyclohexane	C <sub>19</sub> H <sub>38</sub>	9.49	-	-	Insoluble	+ (Koma et al. 2003; Jimenez and Bartha 1996; Koma et al. 2001)
Pristane	C <sub>19</sub> H <sub>40</sub>	9.38	-	-	-	+ (Lee and Cho 2008 ; Nhi-Cong et al. 2009; Abed and Köster 2005)
Phytol	C <sub>20</sub> H <sub>40</sub> O	8.3 à 9.1	-	-	-	+ (Rontani et al. 1999)
Isophytol	C <sub>20</sub> H <sub>40</sub> O	8.2 à 9.1	-	-	Insoluble	+ (Rontani et al. 1999)
Di-2-ethylhexyl-adipate	C <sub>22</sub> H <sub>42</sub> O <sub>4</sub>	8.1	1.38 10 <sup>-2</sup>	3.09 10 <sup>-2</sup>	Insoluble (7.8 10 <sup>-4</sup> )	+ (Barnabe et al. 2008)
Cis-9-Tricosene	C <sub>23</sub> H <sub>46</sub>	11.42	-	-	0.0003	+ (Fritsche W. and Hofrichter M. 2005)
Diocetyl phthalate/ Di(2-ethylhexyl)phthalate	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	7.6 à 8.39	7.49 10 <sup>-2</sup>	3.26 10 <sup>-2</sup>	Insoluble (2.7 10 <sup>-4</sup> )	+ (Barnabe et al. 2008; Liang et al. 2008)
Bis(ethylhexyl)sebacate	C <sub>26</sub> H <sub>50</sub> O <sub>4</sub>	10.08	-	-	< 0.1	+ (MacLeod and Daugulis 2003)
Squalene	C <sub>30</sub> H <sub>50</sub>	14.12	-	-	Insoluble	+ (Rontani J.F. et al. 2002)

Squalane	$C_{30}H_{62}$	14.63	$3.50 \cdot 10^{-2}$	$2.93 \cdot 10^{-2}$	-	+ (Berekaa and Steinbüch 2000)
Trioctyl trimellitate	$C_{33}H_{54}O_6$	11.59	-	-	Insoluble	+
Silicone oil 1-Poly-(dimethyl)-siloxane 2-poly-(methylphenyl)-siloxane	$(C_2H_6SiO)_n/$ $(C_8H_{14}O_2Si_2)_n$	2.6 to 4.25	0.005 to 0.2	-	Insoluble	– (Darracq et al. 2010c; Déziel et al. 1999; Muñoz et al. 2007; Quijano et al. 2009; Guieysse et al. 2001; Ascon-Cabrera and Lebeault 1995)
Paraffin oil	-	-	-	-	Insoluble	+ (Oliveira and De França 2005)
Fluorocarbone 40 (43) FC 70	$C_9F_{21}N$ ( $C_{12}F_{27}N$ ) $C_{15}F_{33}N$	(9.98) 12.88	-	-	Insoluble	– (Césario et al. 1997a; Césario et al. 1997b)
CO-1214 fatty Alcohol	$CH_3(CH_2)_{n-2}CH_2-OH$ $n = 10 \text{ à } 12$	5.2	0.012 at 30°C	-	Insoluble	+ (Kester and Foster 1963)
Corn oil	-	7.4	-	-	Insoluble	+ (L. Singh et al. 2000)

<sup>a</sup>+ biodegradable, – non-biodegradable

\* Cost according to Acros Organics

**Table 10.** Critical log  $K_{ow}$  for various microorganisms

Microorganisms	Gram	Critical log $K_{ow}$	References
<i>Bacillus</i> OS-1906	+	2.0	(Sardessai and Bhosle 2002)
<i>Arthrobacter</i> S-1	+	2.0	(Sardessai and Bhosle 2002)
<i>Pseudomonas putida</i> S12	-	2.3	(Sardessai and Bhosle 2002)
<i>Pseudomonas. aeruginosa</i> LST-03	-	2.9	(Ogino et al. 1999)
<i>Pseudomonas</i> sp. ATCC 55595	-	3.1	(Collins and Daugulis 1999b)
<i>Pseudomonas</i> sp. ATCC 11172	-	3.3	(Vrionis et al. 2002)
<i>Zymomonas mobilis</i>	-	4.0	(Bruce and Daugulis 1991)
<i>Sphingomonas aromaticivorans</i> B065	-	4.0	(Janikowski et al. 2002)
<i>Saccharomyces cerevisiae</i>	-	5.7	(Bruce and Daugulis 1991)
<i>Clostridium acetobutylicum</i>	+	6.0	(Bruce and Daugulis 1991)
<i>Mycobacterium</i> PYR-1	+	7.0	(MacLeod and Daugulis 2003)

**Table 11.** Specific toluene partition coefficient between NAPL and water ( $K_{NAPL/W}$ )

NAPL	$K_{NAPL/W}$	References
Fluorocarbon FC40	17.5	(Césario et al. 1997b)
Octanol	398	(Muñoz et al. 2007)
Oleyl Alcohol	405	(Collins and Daugulis 1999a)
Dipentyl ether	473	(Collins and Daugulis 1999a)
2-Decanol	745	(Collins and Daugulis 1999a)
Jasmone	1240	(Collins and Daugulis 1999a)
2-Undecanone	1304	(Collins and Daugulis 1999a)
2-Decanone	1384	(Collins and Daugulis 1999a)
1-Decyne	1587	(Collins and Daugulis 1999a)

**Table 12.** Examples of bioreactor experiments involving polydimethylsiloxane (PDMS) either as an absorbent or a tank for pollutants.

Treatment or process	Compounds	Microorganisms	Viscosity	Main conclusions	References
Absorption	Oxygen	-	25 mPa.s	High solubility in PDMS and equilibrium solubility of the same order of magnitude as hydrocarbons	(Cannon et al. 1960)
Two-phase partitioning bioreactor	Di- and tri-chlorobenzene Ethylbutylaldéhyde Ethyl butyrate Ethanol Ethyl acetate	Mixed culture (activated sludge)	19 mPa.s	Microbial growth on all substrate mixtures 45% biomass located at the oil/water interface around the oil drops Silicon oil non-biodegradable Efficient system to remove toxic and hydrophobic compounds	(Ascon-Cabrera and Lebeault 1993)
Two-phase partitioning bioreactor	PAH: pyrene, perylene, chrysene	Mixed culture	4.6 mPa.s and 19 mPa.s	Silicon oil is relevant for multiphase bioreactor (hydrophobic, chemically stable and resistant to biodegradation) Addition of surfactant is not interesting because they are readily biodegradable leading to substrate competition. Degradation principally occurs at the oil/water interface	(Marcoux et al. 2000)
Two-phase partitioning bioreactor	Phenanthrene and pyrene	Mixture of <i>Pseudomonas sp</i> and <i>Sphingomonas sp</i>	2 mPa.s	PDMS relevant for TPPB Bacterial adhesion at the interface and improved degradation rates Two-phasic system improves the pollutant dispersion and mass transfer between both liquid phases	(Guieysse et al. 2001)
Biofiltration	Hexane	Activated sludge	265 mPa.s	Comparison between biofilters with and without PDMS. No clear trend showed.	(Fazaelipoor and Shojaosadati 2002)
Absorption	Oxygen	-	4.6 mPa.s	O <sub>2</sub> solubility in PDMS 8 times higher than in water	(Dumont et al. 2006)
Absorption Two-phase partitioning bioreactor	Hexane	<i>Pseudomonas aeruginosa</i>	19 mPa.s	Hydrophobic compounds show a better affinity for PDMS than for water. Addition of PDMS increases the process performance (RE* and EC* five times higher than in the absence of PDMS) PDMS increases mass transfer in the gas-liquid contactor PDMS has antifoaming properties leading to an absence of foaming	(Muñoz et al. 2006)

Two-phase partitioning bioreactor	Pyrene	<i>Mycobacterium frederiksbergense</i>		Significant yield of degradation and lag time varied with the initial concentration Kinetic model for pyrene degradation is based on an exponential growth	(Mahanty et al. 2008)
Absorption Two-phase partitioning bioreactor	Isopropylbenzene	<i>Rhodococcus erythropolis</i>	47.5 mPa.s	The addition of a co-substrate (ethanol) in the bioreactor enhances VOC removal	(Aldric and Thonart 2008)
Absorption Two-phase partitioning bioreactor	Isopropylbenzene and Oxygen	-	9.4, 96.4, 336 and 1300 mPa.s	Oxygen mass transfer decreases when silicon oil fraction increases; if agitation speed and gas flow increase, $K_{La}$ increases. Viscosity affect gas-liquid mass transfer	(Aldric et al. 2009a)

\*RE: Removal efficiency

\*EC: Elimination capacity

**Table 13.** Various anions in the structure of ionic liquids

Anion	Name	Abbreviation
$\text{BF}_4^-$	Tetrafluoroborate	$[\text{BF}_4]$
$\text{PF}_6^-$	Hexafluorophosphate	$[\text{PF}_6]$
$\text{Cl}^-$	Chloride	$[\text{Cl}]$
$\text{CH}_3\text{CO}_2^-$	Acetate	$[\text{Ac}]$
$\text{CF}_3\text{CO}_2^-$	Trifluoroacetate	$[\text{TFA}]$
$\text{CH}_3\text{SO}_4^-$	Methylsulfate	$[\text{MeSO}_4]$
$\text{CF}_3\text{SO}_3^-$	Trifluoromethylsulfonate	$[\text{TFO}]$
$(\text{CF}_3\text{SO}_2)_2\text{N}^-$	Bis[(trifluoromethyl)sulfonyl]amide	$[\text{NTF}_2]$



**Table 14.** Effects of the positive and negative ions on the physicochemical properties of ionic liquids (Huddleston et al. 2001; Matsumoto et al. 2004; Yang and Pan 2005; Zhao et al. 2007; Docherty et al. 2007)

Properties	Negative ions	Positives ions	
		Base	Alkyl-chains R1 and R2
Polarity and solubility in water	$\text{Cl}^- > \text{I}^- > \text{BF}_4^- > \text{PF}_6^- > \text{NTF}_2^-$	Alkylammonium > Pyrrolidinium > pyridinium > imidazolium	-butyl > -hexyl > -octyl
Viscosity	$\text{Cl}^- < \text{I}^- < \text{BF}_4^- < \text{PF}_6^- < \text{CH}_3\text{CO}_2^- < \text{NTF}_2^-$	Imidazolium > Pyrrolidinium > Alkylammonium	-butyl < -hexyl < -octyl
Toxicity	Cytotoxic negative ions : $[\text{C}_{12}\text{H}_8\text{BO}_4]^-$ , $[\text{PF}_{18}\text{C}_6]^-$ , $[\text{PF}_{24}\text{C}_9]^-$ , $[\text{NF}_6\text{C}_2]^-$ , $\text{SbF}_6^-$ , $\text{Co}(\text{CO})_4^-$ , $[\text{PF}_{10}\text{C}_4\text{O}_2]^-$ , $[\text{NC}_2\text{F}_6\text{S}_2\text{O}_4]^-$ , $[\text{BC}_4\text{O}_8]^-$ et $[\text{C}_4\text{S}_3\text{F}_9\text{O}_6]^-$	Imidazolium > Pyridinium then Alkylphosphonium > Alkylammonium	-butyl < -hexyl < -octyl
Density	$\text{N Tf}_2^- > \text{PF}_6^- > \text{C}_3\text{F}_7\text{CO}_2^- > \text{CF}_3\text{SO}_3^- > \text{CF}_3\text{CO}_2^- > \text{BF}_4^- > \text{Cl}^-$	-	-butyl > -hexyl > -octyl
Surface tension	-	-	-butyl > -hexyl > -octyl
Biodegradability	No specific effect	A little effect, pyridinium > imidazolium	-butyl < -hexyl < -octyl <<< carbonyl or ester groups
Biocompatibility	-	-	-butyl > -hexyl > -octyl