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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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Abstract

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

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

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1. Introduction

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

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

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

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

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

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

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

2. The considered integrated process

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

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

The NAPL plays two functions:

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

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

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

Zhang et al. (Y. Zhang et al. 2007) (0.20 g DMS.m^{-3}.h^{-1} or 0.10 gS.m^{-3}.h^{-1}), and by Shu and Chen (Shu and Chen 2009) (90 gS.m^{-3}.h^{-1}).
Similarly to toluene, experimental conditions have also an effect on the removal capacity, namely the considered microorganisms (fungi, pure culture, mixed culture...), the relative humidity of the gas phase, the residence time and the environmental conditions.
The main downsides of biofiltration are:
- the long starting period corresponding to cell proliferation in the bed (Daugulis 2001),
- the sensibility of the process versus a lot of environmental conditions (Kennes et al. 2009),
- the biofilter volume and hence its built-up area.

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

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

3. Absorption of hydrophobic VOC

3.2. Mass transfer theory

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

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

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

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

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

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

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

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

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

With Q_G and Q_L the gas and liquid volumetric flow rates (m^3.s^{-1}), and ΔC_{ML}, the average logarithmic concentration of the pollutant in the liquid phase (mol.m^{-3}).

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

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

3.2. Henry's constants

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

$$C_G = HC_L \quad (4)$$

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

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

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

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

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

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

3.3. Global mass transfer coefficient

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

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

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

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

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

3.4. Diffusion coefficient

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

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

3.5. NAPL viscosity

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

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

4. Regeneration of the Non-Aqueous Phase Liquid by biodegradation

4.1. Two-phase partitioning bioreactor (TPPB)

After VOC mass transfer from the gas phase to a NAPL, VOC degradation is carried out in a two-phase partitioning bioreactor (TPPB), which consists of a stirred bioreactor filled with two immiscible liquid phases, leading to the formation of an emulsion, increasing the interfacial area. This concept is based on the selective partitioning of the pollutant between water and NAPL. VOC biodegradation performances depend on the presence and the assimilation potential of various microbial agents such as bacteria, fungi or yeasts in the aqueous phase (Rehmann and Daugulis 2007). In a TPPB, hydrophobic (or toxic) compounds are delivered to the aqueous phase at sub-inhibitory levels for microorganisms in case of toxic compounds or at the solubilisation limit in case of hydrophobic compounds, related to the microbial demand.
Déziel et al. (Déziel et al. 1999) proposed three mechanisms for hydrophobic or toxic compounds consumption:

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

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

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

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

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

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

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

4.2. Toxicity of NAPL towards microorganisms or biocompatibility

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

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

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

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

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

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

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

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

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

4.3. Miscibility of NAPL in water

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

4.4. Biodegradability of NAPL

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

5. Screening and choice of the NAPL

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

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

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

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

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

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

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

- HMN (2,2,4,4,6,8,8-Heptamethylnonane) owing to the presence of terminal methyl groups. Some authors showed the resistance of HMN to biodegradation by *Arthrobacter* (Efroymson and Alexander 1991) or mixed cultures (Ghoshal et al. 1996; Kirkwood et al. 2008); while marine microbial community would be able to degrade HMN (Rontani and Giusti 1986).

- Fluorocarbon FC 40 has been tested by Césario et al. (Césario et al. 1998), who could not put its biodegradation in evidence. However, recent reports questioned on the high volatility of this compound and its high power of depletion on ozone (Quijano et al. 2009).

- Polymers are potentially usable in a TPPB. The polyisobutylene is recalcitrant towards microorganisms (Alexander 1973) since constituted of many terminal methyl groups. However, the viscosity of this polymer is high and will increase the pressure drop in the gas/liquid contactor, and/or the stirred power needed in order to create a maximal interfacial area to improve the transfer in the aqueous phase. In this case, the process consumes a large amount of energy.

- Silicone oil (polymethylsiloxane or PDMS) has been used by several authors (Ascon-Cabrera and Lebeault 1993, 1995; Bouchez et al. 1995; Gardin et al. 1999; Fazaelipoor and Shojaosadati 2002; Aldric et al. 2009a) as an absorbent and a pollutant tank in a multiphase bioreactor. Among the various polymers of this family, all are potentially usable as NAPL in TPPB, owing to their commonly accepted absence of biodegradability. They should be, however, considered with circumspection due to the following general features, a high viscosity and a solid state at ambient temperature.

- The last class of compounds concerns ionic liquids (IL), which are more or less biodegradable, depending on their structure.

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

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

5.1. Silicone oils

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

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

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

In this kind of bioreactors, several authors working with silicone oil (Ascon-Cabrera and Lebeault 1993; Osswald P. et al. 1996) noticed a modification of bacterial behaviour due to cell adhesion to the oil leading to a higher interfacial area; the consequence is a more important dispersion of the NAPL and hence an 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 BmimPF6 (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 (BmimPF6) 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

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Figure captions

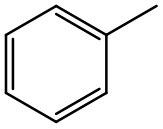
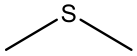
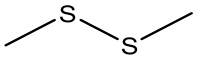
Figure 1. Procedure for the choice of the process to be implemented for loaded VOC air treatment (Smeets, 2002)

Figure 2. Hybrid absorption-biodegradation process with regeneration of the organic phase

Figure 3. Mass transfer phenomena in a two-phase partitioning bioreactor

Figure 4. Structure of silicone oils (a), polydimethylsiloxane (PDMS) and polymethylphenylsiloxane (PMPS), as well as that of ionic liquids (b) with various

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

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

[a]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	*Pseudomonas* sp., *Alcaligenes xylosoxidans*, mixed culture	Oleyl alcohol, hexadecane, DEHA*	(Collins and Daugulis 1999a, 1999b, 1999c; Daugulis and Boudreau 2003; Darracq et al. 2009)
	Benzene	*Kledsiella* sp.	Octadecene	(Yeom and Daugulis 2001b)
		Achromobacter xylosoxidans	Hexadecane	(Nielsen et al. 2005)
		Pseudomonas putida	n-Hexadecane	(D. Singh and Fulekar 2010)
	Xylene	*Pseudomonas* sp.	Oleyl alcohol	(Collins and Daugulis 1999b)
PAH*	Pyrene	*Mycobacterium frederiksbergense*	Silicone oil	(Mahanty et al. 2008; Mahanty et al. 2010)
	Various PAHs	*Mycobacterium*	Bis(ethylhexyl)sebacate	
		Sphingomonas sp.	Dodecane	(MacLeod and Daugulis 2005)
	Naphtalene,	*Pseudomonas* sp*., Bacillus*	Decane, Octadecane, hexane	
	Phenanthrene	*Pseudomonas* sp*.*	Silicon oil, HMN	(Janikowski et al. 2002)
		Mixed culture	Hexadecane, dibutylphtalate	(Abe et al. 1995)
	Various PAHs	Bacteria consortium	Silicone oil, Paraffin oil, HMN*	(Bouchez et al. 1995) (Birman and Alexander 1996) (Marcoux et al. 2000; Vannek et al. 1995)
Alkanes, Alkenes	Hexane,	*Pseudomonas aeruginosa*	Silicone oil	(Muñoz et al. 2006)
	Styrene,	Mixed culture	Silicone oil	(Osswald P. et al. 1996)
	Ethene	*Micobacterium parafortuitum*	Fluorocarbon 40	(Césario et al. 1998)
	α-pinene	Mixed culture	Silicone oil	(Montes et al. 2011)
Sulphur compounds	DMS, DMDS	Mixed culture	DEHA	(Darracq et al. 2009, 2010b)
Chlorinated compounds	2,4,6-trichlorophenol	*Pseudomonas 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

				Lebeault 1993)
Other molecules	Phenol	*Pseudomonas putida*	2-undecanone	(Collins and Daugulis
	Decahydronaphtalene	*Rhodococcus* spp.	HMN	1997a, 1997b)
	4-nitrophenol	Mixed culture	Undecanol, 2-undecanone, oleyl alcohool	(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
Design	One reactor (open)	One reactor (closed)	Two reactors	Two reactors
Liquid absorbent	Water	Water	Water	NAPL
Solid phase for absorption	Natural filter bed or inert	Exclusively inert packing materials	Inert packing materials	Inert packing materials
Composition of liquid	Water with microorganisms and nutriments	Water	Water	Organic Solvent or emulsion water/NAPL
Surface area	High	Low	Low	Low
Concentration of pollutants and example	< 1 $g.m^{-3}$ Toluene, DMS, Styrene, □-pinene, H_2S, Methanol	< 0.5 $g.m^{-3}$ Ethanol, Ammonia, DMS, H_2S, Phenol, Trichloroethylene	< 5 $g.m^{-3}$ H_2S, SO_2, Alcohols, aldehydes, Amines, Odours	< 0.1 $g.m^{-3}$ Hexane, Toluene, Dichloromethane, styrene
Suitable for compounds with Henry's constant in water ($Pa.m^3.mol^{-1}$)	< 1	< 0.1	< 0.01	> 1 in water
Biomass	Fixed	Fixed	Suspension	Suspension
Clogging of packing	Problem	Problem	No problem	No problem
Advantages	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	Medium acidification Media degradation, high built-up area, high pressure drop increase and low removal efficiency Compulsory humidification of the gas effluent Biodegradation increases medium temperature Specific inoculums required to treat recalcitrant compounds Absorption/desorption cycles Operating conditions (pH, Humidity, water activity, temperature, etc) Risk of anaerobic zones	High L/G ratio, so operation cost increase and biofilm detachment Higher residence time in reactor for recalcitrant compounds than for readily biodegradable pollutants Biomass accumulation leading to pressure drop increase Non-homogenous biomass distribution	Low residence time in packed column which does not allow hydrophobic VOC absorption Biomass accumulation, so increase of pressure drop but the high liquid flow rates minimise growth in the scrubber	Pollutants degraded in the aqueous phase Difficult to find a NAPL non biodegradable and easy to regenerate Viscous NAPL increase the pressure drop in the absorber High stirring energy for aeration and agitation

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

VOC	H ($Pa.m^3.mol^{-1}$)	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)
	604	293	(Staudinger and Roberts 2000)
o-Xylene	500	298	(Mackay and Shiu 1981)
	390	293	(Staudinger and Roberts 2000)
m-Xylene	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 (Pa.m^3.mol^{-1}) or water/NAPL emulsions

	VOC		
NAPL (viscosity)	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

	VOC			
Solvents	Toluene	DMS	DMDS	References
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 ($m^2.s^{-1}$) in various liquid absorbents

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

[a]Estimated according to Wilke and Chang (Wilke and Chang 1955)

[b]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 ($g.m^{-3}.h^{-1}$)	References
33% Oleyl alcohol	*Pseudomonas* sp.,	79	(Collins and Daugulis 1999c)
33% n-Hexadecane	*Alcaligenes xylosoxidans*	733	(Daugulis and Boudreau 2003)
	Achromobacter xylosoxidans	>326	(Boudreau and Daugulis 2006)
6% 2-Undecanone	*Pseudomonas putida*	197	(Hamed et al. 2004)
100% water	Mixed culture aquifer	0.96	(Alvarez and Vogel 1991)
	Pseudomonas 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 ($g.L^{-1}$)	Biodegradability[a]
Cyclohexane	C_6H_{12}	3.2 à 3.44	$9.66\ 10^{-4}$	$2.53\ 10^{-2}$	0.058	+ (Lee and Cho 2008)
Hexane	C_6H_{14}	3.29	$3.10\ 10^{-4}$	$1.85\ 10^{-2}$	0.013	+ (Lee and Cho 2008)
Ethylene glycol diehyl ether	$C_6H_{14}O_2$	0.77	$7.27\ 10^{-4}$	$2.43\ 10^{-2}$	20.4% en volume	+
Cyclooctene	C_8H_{14}	3.79	$1.66\ 10^{-3}$	$2.94\ 10^{-2}$	-	+ (Collins and Daugulis 1999a)
Isooctane	C_8H_{18}	4.09	$5.07\ 10^{-4}$	$1.88\ 10^{-2}$	Insoluble	+ (Solano-Serena et al. 2004)
Ethyl heptanoate	$C_9H_{18}O_2$	3.4	-	$2.78\ 10^{-2}$	0.29	+
(+)-Limonene	$C_{10}H_{16}$	4.1 à 4.83	-	-	$1.38\ 10^{-2}$	+ (Janikowski et al. 2002; Van der Werf et al. 1999)
1-Decyne	$C_{10}H_{18}$	4.67	$1.32\ 10^{-3}$	$2.62\ 10^{-2}$	-	+
Decene	$C_{10}H_{20}$	5.19	$8.20\ 10^{-4}$	$2.48\ 10^{-2}$	$1.48\ 10^{-4}$	+ (Vieira et al. 2007)
2,6-dimethyl-2-octene	$C_{10}H_{20}$	5.02	-	-	-	+ (Fall et al. 1979)
2-Decanone	$C_{10}H_{20}O$	3.2 to 3.7	-	-	$7.68\ 10^{-2}$	+ (Collins and Daugulis 1999a)
Décane	$C_{10}H_{22}$	5.25	$9.30\ 10^{-4}$	$2.39\ 10^{-2}$	-	+ (Fritsche W. and Hofrichter M. 2005; Kester and Foster 1963)
3,6-dimethyloctane	$C_{10}H_{22}$	5.1 to 5.9	-	-	-	+ (Fall et al. 1979)
1-decanol	$C_{10}H_{22}O$	3.8 to 4.6	$1.39\ 10^{-2}$	$2.88\ 10^{-2}$	Insoluble	+ (Kester and Foster 1963)
Dipentyl ether	$C_{10}H_{22}O$	3.96	$1.08\ 10^{-3}$	$2.48\ 10^{-2}$	Insoluble	+
2-Decanol	$C_{10}H_{22}O$	3.9	-	-	-	+ (Collins and Daugulis 1999a)
Jasmone	$C_{11}H_{16}O$	3.55 to 4.1	-	-	0.168	+ (Collins and Daugulis 1999a)
2-Undecanone	$C_{11}H_{22}O$	3.69 à 4.09	-	-	$1.97\ 10^{-2}$	+ (Fritsche W. and Hofrichter M. 2005)
Undecane	$C_{11}H_{24}$	5.74	$1.20\ 10^{-3}$	$2.47\ 10^{-2}$	Insoluble	+ (Kester and Foster 1963)
2-dodecanone	$C_{12}H_{24}O$	4.4	-	-	-	+ (Collins and Daugulis 1999a)
Dodecanal	$C_{12}H_{24}O$	4.7	$2.04\ 10^{-3}$	$2.94\ 10^{-2}$	Insoluble	+ (Fritsche W. and Hofrichter M. 2005)
Dodecane	$C_{12}H_{26}$	6.23	$1.15\ 10^{-3}$	$2.54\ 10^{-2}$	Insoluble ($3.66\ 10^{-6}$)	+ (Sáez-Navarrete et al. 2008)
Diethylsebacate	$C_{14}H_{26}O_4$	4.33	-	-	0.08	+ (Nalli et al. 2006; Barnabe et al. 2008)

Tetradecane	$C_{14}H_{30}$	7.2	$2.34\ 10^{-3}$	$2.66\ 10^{-2}$	Insoluble	+ (Kester and Foster 1963)
Farnesol	$C_{15}H_{26}O$	5.4	-	-	Insoluble	+ (Berekaa and Steinbüch 2000; Seubert 1960)
Dibutylphtalate	$C_{16}H_{22}O_4$	4.5 à 4.7	$2.13\ 10^{-2}$	$3.32\ 10^{-2}$	0.13	+ (Eaton and Ribbons 1982)
Ethyl Myristate	$C_{16}H_{32}O_2$	6.9	-	-	Insoluble	+
HMN or 2,2,4,4,6,8,8-heptamethylnonane	$C_{16}H_{34}$	7.79	$3.76\ 10^{-3}$	$2.53\ 10^{-2}$	-	+ (Rontani and Giusti 1986)
n-Hexadecane	$C_{16}H_{34}$	8.2	$1.18\ 10^{-4}$	$2.76\ 10^{-2}$	Insoluble	+ (Fritsche W. and Hofrichter M. 2005; Muñoz et al. 2006)
Isopryl myristate	$C_{17}H_{34}O_2$	7.17	$5.60\ 10^{-3}$	$2.80\ 10^{-2}$	Insoluble	+ (MacLeod and Daugulis 2003)
Linoleic Acid	$C_{18}H_{32}O_2$	7.3 à 7.5	$2.31\ 10^{-2}$	$3.26\ 10^{-2}$	Insoluble	+ (Kester and Foster 1963)
Octadecane	$C_{18}H_{34}$	9.18	$3.87\ 10^{-3}$ at 29°C	$2.77\ 10^{-2}$	Insoluble	+ (Fritsche W. and Hofrichter M. 2005)
1-Octadecene	$C_{18}H_{36}$	9.04	$4.31\ 10^{-3}$	$2.85\ 10^{-2}$	Insoluble	+
Olehyl alcohol	$C_{18}H_{36}O$	7.5	-	-	Insoluble	+ (Fritsche W. and Hofrichter M. 2005)
Trihexylamine	$C_{18}H_{39}N$	7.4 à 7.8	-	-	Insoluble	–
Tridecylcyclohexane	$C_{19}H_{38}$	9.49	-	-	Insoluble	+ (Koma et al. 2003; Jimenez and Bartha 1996; Koma et al. 2001)
Pristane	$C_{19}H_{40}$	9.38	-	-	-	+ (Lee and Cho 2008 ; Nhi-Cong et al. 2009; Abed and Köster 2005)
Phytol	$C_{20}H_{40}O$	8.3 à 9.1	-	-	-	+ (Rontani et al. 1999)
Isophytol	$C_{20}H_{40}O$	8.2 à 9.1	-	-	Insoluble	+ (Rontani et al. 1999)
Di-2-ethylhexyl-adipate	$C_{22}H_{42}O_4$	8.1	$1.38\ 10^{-2}$	$3.09\ 10^{-2}$	Insoluble ($7.8\ 10^{-4}$)	+ (Barnabe et al. 2008)
Cis-9-Tricosene	$C_{23}H_{46}$	11.42	-	-	0.0003	+ (Fritsche W. and Hofrichter M. 2005)
Dioctyl phthalate/ Di(2-ethylhexyl)phtalate	$C_{24}H_{38}0_4$	7.6 à 8.39	$7.49\ 10^{-2}$	$3.26\ 10^{-2}$	Insoluble ($2.7\ 10^{-4}$)	+ (Barnabe et al. 2008; Liang et al. 2008)
Bis(ethylhexyl)sebacate	$C_{26}H_{50}O_4$	10.08	-	-	< 0.1	+ (MacLeod and Daugulis 2003)
Squalene	$C_{30}H_{50}$	14.12	-	-	Insoluble	+ (Rontani J.F. et al. 2002)

Squalane	$C_{30}H_{62}$	14.63	$3.50\ 10^{-2}$	$2.93\ 10^{-2}$	-	+ (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 à 12	5.2	0.012 at 30°C	-	Insoluble	+ (Kester and Foster 1963)
Corn oil	-	7.4	-	-	Insoluble	+ (L. Singh et al. 2000)

[a] + biodegradable, – non-biodegradable

[*] Cost according to Acros Organics

Table 10. Critical log *Kow* for various microorganisms

Microorganisms	Gram	Critical log *Kow*	References
Bacillus OS-1906	+	2.0	(Sardessai and Bhosle 2002)
Arthrobacter S-1	+	2.0	(Sardessai and Bhosle 2002)
Pseudomonas putida S12	−	2.3	(Sardessai and Bhosle 2002)
Pseudomoans. aeruginosa LST-03	−	2.9	(Ogino et al. 1999)
Pseudomonas sp. ATCC 55595	−	3.1	(Collins and Daugulis 1999b)
Pseudomonas sp. ATCC 11172	−	3.3	(Vrionis et al. 2002)
Zymomonas mobilis	−	4.0	(Bruce and Daugulis 1991)
Sphingomonas aromaticivorans B065	−	4.0	(Janikowski et al. 2002)
Saccharomyces cerevisae	−	5.7	(Bruce and Daugulis 1991)
Clostridium acetobutylicium	+	6.0	(Bruce and Daugulis 1991)
Mycobacterium 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 *Pseudomonas sp* and *Sphingomonas sp*	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_2 solubility in PDMS 8 times higher than in water	(Dumont et al. 2006)
Absorption Two-phase partitioning bioreactor	Hexane	*Pseudomonas aeruginosa*	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	*Mycobacterium frederiksbergense*		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	*Rhodococcus erythropolis*	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
BF_4^-	Tetrafluoroborate	$[BF_4]$
PF_6^-	Hexafluorophosphate	$[PF_6]$
Cl^-	Chloride	[Cl]
$CH_3CO_2^-$	Acetate	[Ac]
$CF_3CO_2^-$	Trifluoroacetate	[TFA]
$CH_3SO_4^-$	Methylsulfate	$[MeSO_4]$
$CF_3SO_3^-$	Trifluoromethylsulfonate	[TFO]
$(CF_3SO_2)_2N^-$	Bis[(trifluoromethyl)sulfonyl]amide	$[NTF_2]$

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	$Cl^- > I^- > BF_4^- > PF_6^- > NTF_2^-$	Alkylammonium > Pyrrolidinium > pyridinium > imidazolium	-butyl > -hexyl > -octyl
Viscosity	$Cl^- < I^- < BF_4^- < PF_6^- < CH_3CO_2^- < NTF_2^-$	Imidazolium > Pyrrolidinium > Alkylammonium	-butyl < -hexyl < -octyl
Toxicity	Cytotoxic negative ions : $[C_{12}H_8BO_4]^-$, $[PF_{18}C_6]^-$, $[PF_{24}C_9]^-$, $[NF_6C_2]^-$, SbF_6^-, $Co(CO)_4^-$, $[PF_{10}C_4O_2]^-$, $[NC_2F_6S_2O_4]^-$, $[BC_4O_8]^-$ et $[C_4S_3F_9O_6]^-$	Imidazolium > Pyridinium then Alkylphosphonium > Alkylammonium	-butyl < -hexyl < -octyl
Density	$N Tf_2^- > PF_6^- > C_3F_7CO_2^- > CF_3SO_3^- > CF_3CO_2^- > BF_4^- > Cl^-$	-	-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