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Toluene degradation in a two-phase partitioning bioreactor involving a hydrophobic ionic liquid as a non-aqueous phase liquid

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An ionic liquid (IL), 1-octylisoquinolinium bis(trifluoromethyl-sulfonyl) imide also known as [OctIq][NTf_2], was selected, since it complies with all the requested characteristics to be used as non-aqueous phase liquid (NAPL) in a two-phase partitioning bioreactor (TPPB) dedicated to the biological treatment of the hydrophobic volatile organic compound, toluene. Various operating parameters were investigated and the performances were compared to those recorded in the absence of NAPL. With an aeration flow rate of 0.2 L min^{-1} and in the presence of [OctIq][NTf_2] as NAPL in a TPPB of 12 L, the system allowed to avoid toluene stripping and to totally remove toluene at different concentrations ranging from 0.55 to 1.13 g L^{-1}. However, and even if the ionic liquid addition seemed to decrease the toluene biodegradation rate, higher toluene concentrations could be treated due to the high affinity of toluene for the selected IL. For high toluene concentrations, biodegradation rate might be limited by the oxygen supply because the dissolved oxygen concentration was almost zero. [OctIq][NTf_2] appears to be a suitable NAPL for the biological treatment of toluene. To improve both toluene and oxygen availabilities, the NAPL-to-water ratio should be investigated in order to optimize the interfacial area due to the dispersion of [OctIq][NTf_2] droplets in water, as well as the effect of aeration rate on toluene biodegradation rates.

1. Introduction

The emissions of hydrophobic volatile organic compounds (VOCs) are of the major concerns for the world health organizations and environmental protection offices, due to their odorous character and their toxicity. Because of their hydrophobicity, these compounds can only be removed by specific processes, like adsorption, thermal or catalytic oxidation, or in some cases by conventional bioprocesses such as biofilters, bioscrubbers or biotrickling filters (Gracian et al., 2015; Li and Liu, 2006; Padhi and Gokhale, 2016; Rathnasamy and Kumaresan, 2013; Xue et al., 2013). Chemical scrubbing with an aqueous solution, widely used in the case of odorous gaseous effluents, cannot be used. On the contrary, heavy solvents such as diethylhexyl phthalate (Béchohra et al., 2015), bis(2-ethylhexyl) adipate (Darracq et al., 2009) or silicone oils (Darracq et al., 2009, 2012b) show high affinity towards hydrophobic VOCs; they have been therefore studied in order to be used as a Non-Aqueous Phase Liquid (NAPL) in a two-phase partitioning bioreactor (TPPB) (Arca-Ramos et al., 2014; Béchohra et al., 2014; Collins and Daugulis, 1999; Muñoz et al., 2007) in a promising process coupling absorption and biodegradation. In a first step, the gaseous effluent polluted with hydrophobic VOCs such as toluene, xylene, or dimethylsulfure is absorbed by the NAPL in an absorption column, which is then sent in a TPPB. This kind of bioreactor is based on the concomitant presence of water and NAPL, which improves the targeted pollutant removal (Rols et al., 1990).

As a consequence, NAPL should display the following characteristics: (i) not toxic for microorganisms, (ii) not biodegradable, (iii) water-immiscible, (iv) having a high affinity towards the targeted VOC, (v) a low vapour pressure, (vi) a low viscosity and (vii) an acceptable cost. The use of activated sludge as NAPL should be

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avoided; nevertheless some studies pointed out the specific use of an organic waste as NAPL, which should be therefore biodegradable, in order to simultaneously biodegrade the NAPL and the targeted VOC within the TPPB, e.g. diethylhexyl phthalate and toluene (Béchohra et al., 2015) or decanol and phenol systems (Vrionis et al., 2002) as organic solvent and targeted VOC. Some other results dealing with TPPB are presented in the literature (Aldric and Thonart, 2008; Davidson and Daugulis, 2003; Poleo and Daugulis, 2013; Quijano et al., 2009). Nonetheless, to limit the functioning cost of the process, the solvent must be recovered after the absorption step through a chemical, physical or biological process. Among the available solvents, the non-biodegradability criterion allowed to select two classes of solvents: silicone oils and ionic liquids (IL) (Darracq et al., 2012b; Quijano et al., 2011a). The latter are molten salts having a melting point at or below 100 °C and consist of an organic cation linked to a counter-ion (Welton, 1999; Wilkes, 2002; Wilkes et al., 1982). They appear particularly promising due to their high absorption capacity towards hydrophobic compounds and their negligible saturated vapour pressure; they are also non-flammable and they can be easily be recovered after being used (Earle and Seddon, 2000; Huddleston et al., 1998, 2001). Their physicochemical properties such as lipophilicity, viscosity, density, etc. can be fine-tuned by modifying their chemical structure (e.g. alkyl side chain, organic core or counter anion), which leads to a wide range of possible combinations on a structural point of view (Chiappe and Pieraccini, 2005; Coleman and Gathergood, 2010; Huddleston et al., 2001; Maiti and Rogers, 2011; Quijano et al., 2010; Shkrob and Wishart, 2009; Weingärtner, 2008; Wilkes and Zaworotko, 1992). In a previous work, phenol biodegradation rates in the presence of some phosphonium ionic liquids were found efficient in multiphase reactors (Baumann et al., 2005). Regarding hydrophobic VOCs, $[Bmim][NTf_2]$ and $[Bmim][PF_6]$ have been studied for toluene biodegradation in 120-mL flasks TPPB, assessing the influence of activated sludge acclimation to VOC (Quijano et al., 2009); however further work is required to optimize DMDS degradation in the presence of ILs (Quijano et al., 2011a).

Implementation of ILs in TPPB and their subsequent recycling owing to their cost (relatively more expensive than other NAPL), their non-biodegradability and their biocompatibility are important parameters. The first part of this project consisted in a screening of 23 IL with different cationic scaffolds (imidazolium, isoquinolinium, pyrolidinium, morpholium, triazolium and sulfonium) including functionalized or non-functionalized alkyl side chains and associated with various anions (PF_6^-, NTf_2^- and NfO^-). These IL were synthesized according to classical conditions involving an alkylation reaction with the appropriate halide and an anion exchange. Toxicity against activated sludge and zebrafish *Danio rerio* were assessed, as well as cytotoxicity. Biodegradability and fluoride release in water were also verified in order to avoid possible toxic effects if the hydrophobic IL is discharged into the environment or during handling (Darracq et al., 2012a; Dumont et al., 2012; Rodriguez Castillo et al., 2016d). The toluene biodegradation in $[OctIq][NTf_2]$, $[AllylEt_2S][NTf_2]$, $[DecIq][NTf_2]$ and $[Bmim][NTf_2]$ in the presence of non-acclimated sludge was examined; then, $[OctIq][NTf_2]$ and $[AllylEt_2S][NTf_2]$ were studied as NAPL for toluene biodegradation with activated sludge acclimated to toluene first, and finally to both toluene and IL in 120-mL flasks TPPB (Rodriguez Castillo, 2016). According to these previous results, $[OctIq][NTf_2]$ was found to comply to all the requested characteristics and hence showed that it is a promising NAPL for VOC absorption and implementation in batch TPPB. The objective of this work was therefore the implementation of the selected IL in a 12 L-TPPB containing activated sludge to remove toluene. Toluene was considered as a model hydrophobic VOC compound, owing to its wide use in various industrial activities (Desai and Banat, 1997; Guieysse et al., 2001) and since its biodegradation by activated sludge is widely documented (Béchohra et al., 2014; Darracq et al., 2012a; Daugulis, 2001; Quijano et al., 2011b).

2. Materials and methods

2.1. VOC and solvents

The selected VOC was toluene (M = 92.14 g mol^{-1}; density = 0.870 g cm^{-3}; $T_{boiling}$ = 384 K), with a purity > 99%, which was purchased from Sigma-Aldrich (USA). The ionic liquid used was 1-octylisoquinolinium bis(trifluoromethyl-sulfonyl) imide $[OctIq][NTf_2]$ (Fig. 1); it was synthesized following a previously described methodology (Rodriguez Castillo et al., 2016d). Chemical structure and key physical properties were also previously reported (Rodriguez Castillo, 2016; Rodriguez Castillo et al., 2016d).

The main physicochemical characteristics of $[OctIq][NTf_2]$ ($C_{19}H_{24}F_6N_2O_4S_2$) at 25 °C are a molar weight of 522.53 g mol^{-1}, a density of 1.3282 g cm^{-3} and a viscosity of 451 mPa; the dimensionless and dimensional values of its partition coefficient $H_{Toluene/IL}$ are 0.00022 ($C_g \cdot C_L^{-1}$) and 0.5 (Pa m^3 mol^{-1}) respectively, with C_g the toluene concentration in the gas phase (mol L^{-1} at 20 °C and 1 bar) and C_L the toluene concentration in the liquid phase (mol L^{-1}) (Rodriguez Castillo, 2016).

2.2. Microorganisms and media

The activated sludge (AS) used in this work came from Beaurade municipal wastewater treatment plant of Rennes, France. AS were washed four times with water to remove any nutrients other than those contained in the 'conservation' medium. For growth and conservation, AS were incubated in a 8 L bioreactor, under oxygen flow and fed with the following mineral medium (2 g day^{-1}): peptone, 1.28 g; NH_4Cl, 30.4 g; K_2HPO_4, 0.22 g; CH_3COONa, 280 g and a few drops per month of "Viandox®" (as an additional complex substrate). Microbial dry weight (DW) was used to quantify the amount of microorganism of each essay. A volume of activated sludge (1.0–2.0 mL), previously washed with distilled water and centrifuged to eliminate any residual nutrient from the medium, was placed in a previously weighed pan and put in an oven at 105 °C during 24 h in order to completely dry the sample. Subsequently, the dish was weighed again, and then the activated sludge concentration CDW (g L^{-1}) was determined according to Eq. (1):

$$C_{Dw} = \frac{m_{\text{activated slude dried}} - m_{\text{empty pan}}}{V_{\text{sample}}} \tag{1}$$

Before use, in order to eliminate any additional nutrient other than those contained in the TPPB, AS simples were washed as follows: 1 L of sludge was centrifuged at 4000 rpm for 10 min and the supernatant was removed. Then the pellet was suspended in distilled water was and the operation was repeated twice. The solid was at last suspended in the final mineral culture medium containing (Chikh et al., 2011): NH_4Cl: 1.6 g L^{-1}; KH_2PO_4: 3.4 g L^{-1};

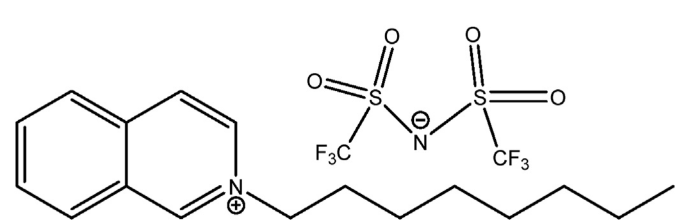

Fig. 1. Structure of the ionic liquid $[OctIq][NTf_2]$.