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Absorption and biodegradation of toluene: Optimization of its initial concentration and the biodegradable non-aqueous phase liquid volume fraction

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ABSTRACT

Di (2-EthylHexyl) Phthalate (DEHP) was selected as a biodegradable organic solvent to be implemented in a two-phase partitioning bioreactor (TPPB) dedicated to remove a model hydrophobic volatile organic compound (VOC), toluene. In a first step, the absorption capacity of toluene in the selected organic solvent was examined according to the partition coefficients H. In a second step, toluene biodegradation in DEHP by non-acclimated activated sludge was carried out for different volume fractions of DEHP in water and five different toluene concentrations (4.3, 43, 106, 212 and 430 mg l^{-1}). Toluene showed high affinity for DEHP with $H = 0.99$ Pa m^3 $mole^{-1}$. Both toluene and DEHP were completely consumed for 4.3 mg l^{-1} (initial toluene concentration) and a volume ratio of 0.1% DEHP in water. For an initial toluene concentration of 106 mg l^{-1} and a volume ratio of 0.1%, total toluene consumption and 87% DEHP degradation yield were obtained after seven days of incubation.

1. Introduction

Removal of volatile organic compounds (VOCs) like toluene is an important issue for human health, as well as for environment. Indeed, many of these compounds are toxic and considered as priority pollutants by the United States Environmental Protection Technology (US-EPA) (Ozturk and Yilmaz, 2006). Various technologies are available to perform their elimination: physical methods, like absorption, adsorption and condensation, and destructive methods, like incineration, catalytic treatment and biological treatment (Heymes et al., 2006; Kraakman et al., 2011). Recently, biological treatments of VOC have been extensively explored as an alternative to conventional methods, like incineration and catalytic treatment, according to the several advantages they offer in comparison to these conventional methods. Indeed, they do not produce any harmful by-products, are probably the most economical techniques for waste air treatment, and are also environment-friendly (Yeom and Daugulis, 2001a; Mudliar et al., 2010). Nevertheless, many VOC are hydrophobic and their removal in biological processes is limited by the difficulty to achieve substrate absorption in an aqueous phase, since microorganisms require water for their growth and hence pollutants transfer from gaseous polluted streams to an aqueous phase is needed (Collins and Daugulis, 1999).

In order to remove hydrophobic compounds such as toluene, benzene and xylene, a promising process consists in the coupling of absorption and biodegradation in a two-phase partitioning bioreactor (TPPB). To improve gas–liquid mass transfer of hydrophobic compounds, the absorbent is a Non-Aqueous Phase Liquid (NAPL) (Déziel et al., 1999; Darracq et al., 2012). Several results dealing with TPPBs are available in the literature (Yeom et al., 2000; Davidson and Daugulis, 2003; Aldric and Thonart, 2008; Quijano et al., 2009). The first step of TPPBs consists of VOC absorption in the NAPL and the second one concerns NAPL regeneration by VOC biodegradation. NAPL improves VOC absorption and at the same time decreases its toxicity towards microorganisms by lowering their concentration in the aqueous phase (Van Groenestijn and Lake, 1999; Tomei et al., 2010).

According to Abu Hamed et al. (2004) the most important criteria in the selection of a NAPL is its biocompatibility (absence of toxicity towards microorganisms), which can be estimated through

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its Log P value. According to Laane et al. (1987), solvents with a log P greater than 4 are generally not toxic. However, NAPL can be attacked by microorganisms: for example (Darracq et al., 2009) found that DEHA was assimilated by activated sludge. Possible NAPL assimilation is especially undesired owing to their significant cost and hence their recycling is important in view of their reuse in a TPPB (Cesário et al., 1998; Darracq et al., 2010). Muñoz et al. (2007) considered 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.

In a previous study (Béchohra et al., 2014), another alternative was tested to overcome this technological lock; a biodegradable solvent (hexadecane) was used as a model solvent. In this case, the solvent should be biodegradable leading to its removal, concomitantly with the target VOC.

In the present work, toluene was chosen as hydrophobic VOC, due to its production in various industrial sectors: fuel, solvent and starting material for the production of plastics, paints, resins, pesticides and dyes (Yeom and Daugulis, 2001b). In view of its subsequent removal in a TPPB, its transfer in a liquid phase should be considered and for this purpose, the chosen solvent must be of low cost, not biodegradable by microorganisms and should have a good capacity to absorb the VOC (Daugulis and Boudreau, 2003). The solvent selected in this study was Di (2-EthylHexyl) Phthalate (DEHP). It is the most used plasticizer among the PVC products. It is considered as a hazardous substance for human health and hence is classified as Category II, by US-EPA, due to its toxicity towards reproduction and development (cancer-causing chemicals classification criteria) (LaGrega et al., 1994). DEHP is released in large amounts in the environment (air, water and soil); the quantities issued are evaluated at 28,653 tons/year in Europe throughout its life cycle, i.e. from production to consumption, and finally as waste (Rank, 2005; Chao et al., 2015).

The aim of this work was therefore to study the biodegradation by activated sludge of the considered VOC in an emulsion of water/DEHP, simultaneously with the biodegradation of the selected organic solvent (DEHP). A particular attention was brought to the optimization of the ratio water/solvent.

2. Material and methods

2.1. Microorganisms and media

The biomass used in this work was activated sludge (AS) from Beaurade, the municipal wastewater treatment plant of Rennes (France). AS was washed four times with water to avoid any nutrients other than those contained in the culture media. The sludge was incubated in an 8 L lab-reactor. For growth and conservation, the activated sludge was cultivated under oxygen flow on the following mineral medium (2 g/day): Peptone, 0.64 g; K_2HPO_4, 0.11 g; NH_4Cl, 15.2 g; CH_3COONa, 140 g and some drops per month of Viandox (as an additional carbon source). Before use, activated sludge was washed several times with distilled water and diluted in a mineral salts medium containing (Chikh et al., 2011): KH_2PO_4: 3.4 g l^{-1}; Na_2HPO_4: 3.09 g l^{-1}; NH_4Cl: 5 g l^{-1}; $MgSO_4$: 0.12 g l^{-1}; $CaCl_2$: 0.05 g l^{-1}; $ZnSO_4$: 0.01 g l^{-1}; $MnSO_4$: 0.01 g l^{-1}; $CuSO_4$: 0.003 g l^{-1}; $(NH_4)_2Fe(SO_4)_2$: 0.1 g l^{-1}. The pH was adjusted to 7 ± 0.2.

2.2. VOC and solvents

The selected VOC was toluene from Carbo Erba reagenti (Peypin, France) and the solvent used was DEHP (MW = 390.60 g mol^{-1}, d = 0.970, $T_{boiling} = -50$ °C) from Acros organic (Geel, Belgium).

2.3. Batch cultures

Experiments were conducted in 250 ml Erlenmeyer flasks closed with cellulosic caps to allow air exchange during the first set of experiments, and then with glass caps equipped with two sampling points sealed with Teflon septum allowing needle introduction. To sample the gaseous phase, a microsyringe with a capacity of 500 μl was used and the sample was injected directly in the gaseous chromatography (GC); aqueous samples were stored in closed vials for further analysis of by-products. The Erlenmeyer headspace was 50 ml. For each experiment, a given number of identical 250 ml Erlenmeyer flasks were considered. Initially a concentration of 4.3 g of toluene per liter of DEHP was tested for four volume ratios DEHP in water: 5%, 2%, 0.5% and 0.1%. Each series of experiments consisted of 13 flasks containing 0.5 g l^{-1} of activated sludge and nutrients as indicated above (see microorganisms and media). A blank test containing the considered amount of DEHP was also carried out to determine the fraction of VOC lost by possible leaks or adsorption on the cellulosic stoppers; its composition was the same as the other flasks except for nutrients and biomass. Stirring was set at 300 rpm and flasks were placed in a thermostated oven (T = 25 °C). Because of the biodegradability and the negligible solubility of DEHP in the aqueous phase, it was not possible to perform a homogenous sampling of the two-phase system and hence a sacrificial method was considered, at predetermined time intervals, duplicate Erlenmeyers were taken for analysis. Gaseous sample was analyzed to quantify the remaining toluene quantity.

2.4. Analytical methods

The toluene concentration in the gas phase was measured by gas chromatography (GC) coupled with a flame ionization detector from Thermo scientific (California, United States). Metabolites formed in the aqueous phase were identified by gas chromatography coupled with mass spectrometry (MS) with headspace (HS) from Perkin Elmer (California, United States). For the quantification of DEHP degradation, an extraction by hexane (25% v/v) coupled to 10 min ultrasonication was performed. The extract was then analyzed by gas chromatography coupled with a flame ionization detector from Perkin Elmer. The analytical conditions are reported in Table 1 and were selected according to the related literature (Chikh et al., 2011; de Moura Carrara et al, 2011).

The toluene partition coefficient in each of the different phases was measured by the static method, by introducing a known amount of toluene in 22 ml vials sealed, having introduced the organic solvent or the emulsion in advance. Then the system was subjected to a fixed rotary shaking at a constant temperature of 25 °C.

The equilibrium was reached after 48 h; toluene concentration in the gas phase was quantified by gas phase chromatography (Table 1). According to the mass balance, toluene concentration in the aqueous phase was then deduced. Then, the dimensionless Henry's constant (H) and Henry's constant (H′) could be calculated by Equations (1) and (2) respectively:

$$H\,C_L = C_G \qquad (1)$$

$$H' = H\,R\,T \qquad (2)$$

R and T are the constant of perfect gas and the working temperature respectively.

The total amount of toluene m_t was then deduced from the mass balance (Equation (3)):