

Absorption of toluene in mixture of organics solvents « DEHP-Hexadecane » followed with biodegradation by activated sludge

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Abstract A mixture of two organic solvents, Di (2-EthylHexyl) Phthalate (DEHP) and Hexadecane, was considered as absorbent for the degradation of toluene at 0.1% by volume of each of the two solvents in order to try to approach a real waste. The partition coefficients of the toluene in the pure mixture and in the "DEHP-hexadecane" emulsion in water were previously measured. The kinetics of degradation has shown that the degradation is rather slow because even after 7 days of cultivation, toluene still persists in the gaseous phase, taking account of the leaks. This can only be due to an oxygen limitation, because the amount of carbon present in the reactor is much greater with the addition of hexadecane (Béchohra *et al.*, 2015)

Degradation rates of DEHP and hexadecane were 68 and 70%, respectively, after seven days and the mineralization rate was only $14.00\% \pm 0.05$. Indeed, on the one hand, the degradation of the three sources of carbon is not complete, and finally, there are a presence of degradation by-products that have not been consumed by the microorganisms.

Keywords: Activated sludges, VOC, Biological treatment, Absorption, biodegradable solvent.

Introduction

Emissions of volatile organic compounds (VOCs) are becoming of increasing regulatory concern. VOCs released into the environment result in environmental damage as pollutants. It is strongly advised not to let the chemical enter into the environment because it persists in the environment (Maeda *et al.*, 2005).

The removal of VOCs is of growing concern. Several techniques are available for treatment of VOCs, One of these methods is absorption, either physical or chemical. For a long time, most of the related reports have been concerning absorption of VOCs in aqueous phases and targeted hydrophilic compounds. Unfortunately,

problematic VOCs are often hydrophobic (benzene, toluene. . .) (Rodriguez Castillo *et al.*, 2016). Therefore, biodegradation of VOCs by pure or mixed cultures of microorganisms has been extensively studied.

Two-phase partitioning bioreactors (TPPBs), which are based on the addition to the biological process of solid or liquid non-aqueous phases (NAPL), can enhance the transfer of hydrophobic VOCs, as a result of the high affinity of the organic phase for these latter, as well as that of O₂. (Van Groenestijn and Lake, 1999; Tomei *et al.*, 2010). To avoid costly NAPL, such as silicone oils and ionic liquids, which showed to be relevant for implementation in a TPPB (Darracq *et al.*, 2010; Dumont *et al.*, 2011; Quijano *et al.*, 2011a, 2011b), but should be recycled owing to their cost, another alternative is to consider an industrial waste containing an organic phase (Chikh *et al.*, 2011; Béchohra *et al.*, 2014).

A biodegradable solvent (Di (2-ethylhexyl) phthalate) (DEHP) in the previous study was tested and found to be efficient for both the absorption capacity step of target VOC "Toluene" and at the biodegradation level, since it is biocompatible, non-soluble in water and biodegradable (Madsen *et al.*, 1999; Feng *et al.*, 2002; Chao and Cheng, 2007; Béchohra *et al.*, 2015).

The hydrophobic targeted VOC is toluene, often encountered in gaseous effluents of pulp and paper factories, composting facilities, food industries or other industries (Rappert and Müller 2005; Jin *et al.* 2007; Darracq *et al.* 2010b).

The impact of the ratio DEHP/water on the biodegradation performances was previously examined, showing an optimum of 0.1 % (volume ratio) for simultaneous degradation of DEHP and toluene (Béchohra *et al.*, 2015, 2016). Indeed, on the one hand, the NAPL quantity must be sufficient to allow a good VOC mass transfer from the organic phase to the aqueous phase. A mixture of two organic solvents was considered as absorbent for the degradation of toluene at 0.1% by volume of each of the two solvents in order to try to approach a real solvent.

1. Material and methods

The selected VOC was toluene and solvent was a mixture of DEHP and Hexadecane. The biomass used in this work was activated sludge (AS) from "Beaurade", the municipal wastewater treatment plant of Rennes (France) and were maintained in a lab-reactor (Chikh *et al.*, 2011; Béchohra *et al.*, 2014)

1.1. Reactor culture

Experiments in a semi-batch reactor (closed for the liquid phase but open for the gas phase) of 2 liters were performed with the same organic solvent (0.1%) and different toluene concentrations in the DEHP (43, 106 and 212 g of toluene / L of DEHP). Stirring was set at 300 rpm in a thermostated bath ($T = 25\text{ }^{\circ}\text{C}$). A blank test without AS was carried out for each concentration to quantify the leakage toluene.

The amounts of toluene in the gas phase, pH and the suspended solid quantity were followed. The sampling of the aqueous phase was also carried out to monitor by-products; the formed CO_2 was also monitored and quantified by a Infrared Fourier Transform (FTIR) brand Environment SA spectrophotometer (Cosma reference Beryl 100).

1.2. 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% volume ratio) coupled to 10 min ultrasonication was performed. The extract was then analyzed by gas chromatography coupled with a flame ionization detector from Perkin Elmer (California, United States).

The total amount of toluene m_t was then deduced from the mass balance (Equation 1):

$$m_t = m_{tg} + m_{te} \quad (1)$$

m_{tg} , m_{te} were the toluene mass in the gaseous and emulsion (DEHP in water) phase at a given time t ; m_{tL} , the toluene leakage, was deduced from the blank test between the initial time and a given time t .

$$m_{tL} = (m_{0gb} + m_{0eb}) - (m_{tgb} + m_{tbe}) \quad (2)$$

m_{0gb} , m_{0eb} were the toluene mass of the blank test in the gaseous phase and the emulsion at initial time m_{tgb} and m_{tbe} were the toluene mass of the blank test at a given time t in the gaseous phase and the emulsion.

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 hours; 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) could be calculated by Equation (3) :

$$H C_L = C_G \quad (3)$$

The concentration in the emulsion (C_e) at a given time t and in the blank test can be then deduced from the partition coefficient H for different volume fractions (Béchohra *et al.*, 2015) and from the toluene concentration in the gaseous phase at the given time t (Eq. 4):

$$C_e = C_G/H \quad (4)$$

The mineralization rate was determined for reactor tests, with and without acclimation; it is defined as the ratio of total carbon moles of CO_2 to the number of moles of carbon consumed or initially introduced with the carbon substrates (Solano-Serena *et al.*, 2001), as represented by equation (5):

$$\% \text{ mineralization} = \frac{n_{C_{CO_2}}}{n_{C_X}} \quad (5)$$

With n_{CO_2} , the total amount of CO_2 -carbon formed and n_{C_X} the total amount of carbon initially introduced.

The biomass growth was quantified by means of turbidimetric measurements at 600 nm which was related to dry matter (DM) through a calibration curve.

2. Results and discussion

The partition coefficients of the toluene in the pure mixture and in the "DEHP-hexadecane" emulsion in water were previously measured. Figure V.32 shows the monitoring of the total amount of toluene over time. It is observed that the degradation is rather slow because even after 7 days of cultivation, toluene still persists in the gaseous phase, taking account of the leaks.

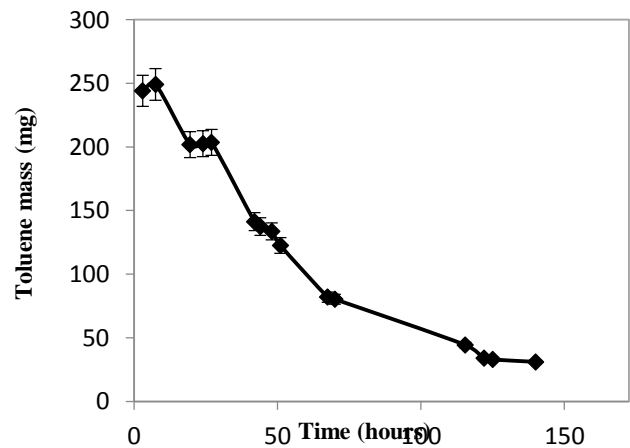


Figure 1. Toluene degradation by non-acclimated sludge in discontinuous reactor with 0,1 % de DEHP-Hexadécane and initial toluene concentration of 106 mg.L⁻¹).

The results obtained by the addition of hexadecane can be explained because, if one compares qualitatively to the test in 5% hexadecane, toluene was consumed more slowly than in 5% DEHP. There is also a non-negligible residual concentration of toluene, which can only be due to an oxygen limitation, because the amount of carbon present in the reactor is much higher with the addition of hexadecane.

Degradation rates of DEHP and hexadecane were 68 and 70%, respectively, after seven days (Figure V.33), and the mineralization rate was only 14.00% ± 0.05. On the one hand, the degradation of the three sources of carbon is not complete, and finally, there are degradation by-products that have not been consumed by the microorganisms (Figure 3).

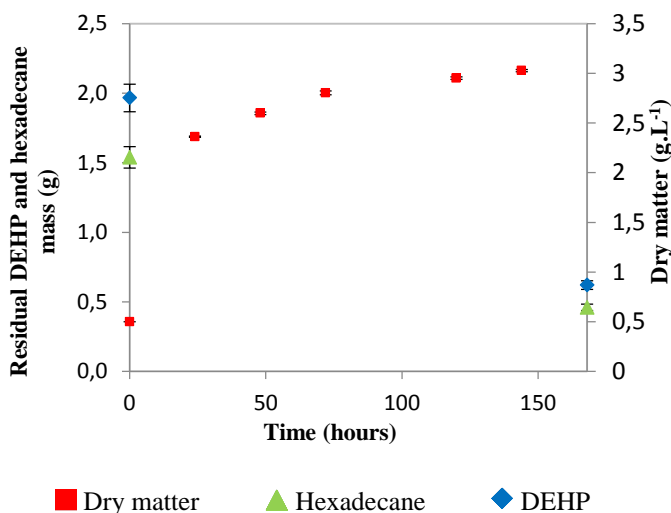


Figure 2. Follow-up of bacterial growth during a culture on non-acclimated activated sludge in batch reactor on 0.1% DEHP-Hexadecane medium (initial concentration of toluene of 106 mg.L⁻¹). Initial and final quantities of hexadecane and DEHP.

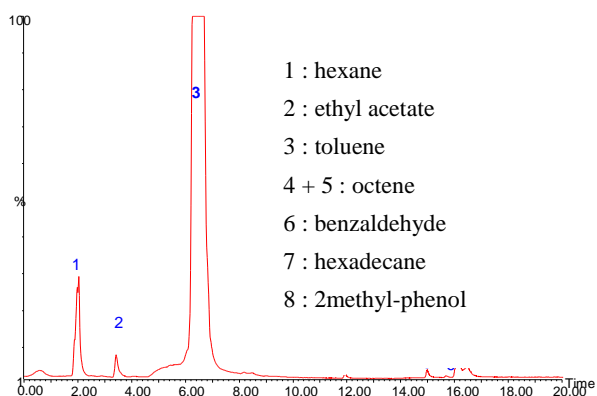


Figure 3. Mass spectrum of the aqueous phase for the test with 106 mg.L⁻¹ of toluene in the hexadecane-DEHP mixture in the reactor.

Conclusion

Biodegradation of toluene in the presence of a mixture of biodegradable solvents (Hexadecane and DEHP) was studied through their impact on the biodegradation yields and rates of carbon sources consumption. 87% of the toluene was degraded in 7 days, which is a longer duration than in the case where only DEHP is used as a solvent, probably Owing to an oxygen limitation. This test makes it possible to envisage the use of a mixture of two or more solvents as absorbents because the actual waste is a mixture of several compounds.

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