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Study on Mass Transfer of Isopropylbenzene and Oxygen in a Two-Phase Partitioning Bioreactor in the Presence of Silicone Oil

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Abstract A two-phase partitioning bioreactor to treat gas effluents polluted by volatile organic compound has been developed. In this work, both the mass transfer of isopropylbenzene (IPB) and oxygen have been considered in relation to their influence on the hydrodynamics of the reactor and the type of silicone oils used as a second phase. The synergistic effect of silicone oil and stirrer speed on the global oxygen mass transfer coefficient (K_La) and gas holdup (up to 12%) have been investigated. The addition of 10% of low viscosity silicone oil (10 cSt) in the reactor does not significantly affect the oxygen transfer rate. The very high solubility of IPB in the silicone oil leads to an enhancement of driving force term, especially for high fraction of silicone oil. However, it does not seem useful to exceed a volume fraction of 10% since K_La_{IPB} decreases sharply at higher proportions of silicone oil. K_La_{IPB} and K_La_{O2} evolve in the same way with the proportion of silicone oil. These results confirm the potentialities of our bioreactor to improve both the oxygen and pollutant gas transfer in the field of the treatment of gaseous pollutants, even for highly concentrated effluents.

Keywords VOC · Two-phase partitioning bioreactor · Mass transfer enhancement · Hydrodynamics · Silicone oil

Introduction

Polluted air has become an increasing environmental and health concern. Numerous polluting organic compounds are released by human activities and persist in the environment because of their insolubility in water and their high concentration.

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Monoaromatic hydrocarbons such as benzene and its derivatives are produced in large amounts and are used in fuels like solvents and as starting materials for the production of plastics, synthetic fibers, and pesticides [1].

Monoaromatics are considered to be persistent environmental contaminants, and 30 of them are on the "EPA Priority Pollutant List" [2]. Eleven of these compounds are in the top 100 chemicals on the "Priority List of Hazardous Substances" published by the Agency for Toxic Substances and Disease Registry [3].

In recent years, biological techniques have been applied more frequently to control these emissions, because they eliminate many of the drawbacks of classical physicochemical techniques. Disadvantages of usual air treatment techniques are high energy costs (incinerators), the use of expensive chemicals that may require special operational safety procedures (chemical scrubbers), and the generation of waste products like spent chemical solutions or spent activated carbon [4, 5]. Biological methods, like biofilters and biotrickling filters, have been recognized as promising alternatives compared to the traditional technologies for the control of many gaseous pollutants [6]. However, biofilters present several limits! On the one hand, the ripening period of the biofilters during which cells proliferate to the point where the bed can be used, when biomass becomes adapted to pollution. On the other hand, biofilters are restricted to the treatment of low volatile organic compounds (VOC) concentration (below 1 g/m^3); this is partly due to the fact that some gaseous pollutants are poorly water soluble.

Earlier, some research had been undertaken in this field to improve mass transfer and solubility of apolar pollutants during biological treatment. Budwill and Coleman [7] have shown the positive effect of the addition of silicone oil on the biodegradation rate of *n*-hexane vapors in peat biofilters. Cesàrio et al. [8] have observed an enhancement in the toluene mass transfer rate by a factor of 1.1 and a twofold oxygen transfer rate using a dispersion containing 10% (*v*/*v*) FC40 solvent.

Recently, many researchers have proposed two-phase partitioning bioreactor (TPPB) as a new treatment alternative for VOC removal [9, 10]. The TPPB concept has been demonstrated to be more effective for the degradation of high levels of organic compounds. Indeed, it has been proven that the use of a nonaqueous phase improves the mass transfer of hydrophobic VOC to the microorganism. The elimination capacity in TPPB exceeds the performances of traditional biofilters for comparable loading rate (Table 1).

The addition of a second phase has an impact on the mass transfer of oxygen but the related effects differ according to the authors. The addition of a second, immiscible liquid phase (hexadecane; 33% *v*/*v*) exhibiting a high oxygen solubility to an aqueous medium increases the oxygen solubility of the system, thus enhancing oxygen mass transfer rate [11]. Dumont and Delmas [20] have reviewed the mechanism of mass transfer enhancement of gas absorption in oil-in-water systems and have concluded that the understanding of the influence of oil addition on the mass transfer parameters K_L and a could be improved. Indeed, there is no explanation about the variation of the interfacial area upon addition of oil at this time: Both increase and decrease in a have been reported. Mass transfer in gas–liquid–liquid systems is difficult to model, mainly due to the droplet distribution inside the boundary layer and the physical properties of the oil used. The driving force to use TPPB for VOC removal has been the presence of organic solvents to trap the hydrophobic contaminant. However, the ability to metabolize the solvent itself could interfere with xenobiotic degradation and thus limit the remediation efficiency [21].

In this work, the use of silicone oil in a two-phase partitioning bioreactor has been studied. Silicone oils has been shown to be safe and compatible with the aqueous phase and

Table 1 Examples of loading rates and elimination capacities quoted in literature for some compounds.

	Compounds	Microorganism	Loading rate (g/m^3 h)	Elimination capacities (g/m^3 h)	Reference
TPPB	Benzene	*Achromobacter xylosoxidans* Y234	143	141	Nielsen et al. [11]
	Hexane	*Pseudomonas aeruginosa*	180	140	Muñoz et al. [12]
	Toluene	*Achromobacter xylosoxidans* Y234	343	325	Boudreau and Daugulis [13]
	Isopropylbenzene	*Rhodococcus erythropolis* T 902.1	450	340	Aldric et al. [14]
	Toluene	*Alcaligenes xylosoxidans*	748	727	Daugulis and Boudreau [15]
Biofilter	Toluene	*Scedosporium apiospermum*	255	250	García-Peña et al. [16]
	Toluene	*Pseudomonas* sp.	238	198	Jacobs et al. [17]
	Hexane	*Fusarium solani*	160	100	Arriaga and Revah [18]
	Styrene	Mixed bacterial culture	473	464	Djeribi et al. [19]

growth of microorganisms (results not shown). Interestingly, the surface tension of silicone oil decreases with viscosity, leading to a better emulsion between the two phases.

This work has focused on the influence of the hydrodynamic conditions on the oxygen mass transfer. Different types of silicone oils have been tested for their influence on both the oxygen and isopropylbenzene (IPB) mass transfer. The latter compound being a volatile organic compound representative was selected among the family of monoaromatic compounds.

Material and Methods

Method for Determination of Oxygen and IPB Mass Transfer Coefficients

The global volumetric mass transfer coefficient, K_La, has been determined, both for oxygen and IPB, by means of the dynamic gassing-out method at 25 °C. For oxygen K_La measurements, dissolved oxygen was first removed from the reactor by sparging with nitrogen until the dissolved oxygen concentration decreased to nearly zero, the nitrogen flow was then stopped. Aeration was started and the airflow rate adjusted to the required value. Once the reactor reached a hydrodynamic steady state by visual inspection (typically <20 s from initiation of aeration), the increase in dissolved oxygen concentration was measured over time until the fluid became saturated with oxygen. Output signals from the dissolved oxygen meters have been logged every 2 s using a data logger (Yokogawa DAQ station DX 106-1-2). The response time of the dissolved oxygen electrodes (~6 s for 63% of full-scale response) was in any case $\leq 1/K_La$ and the probe lag time can thus be neglected. Dissolved oxygen concentrations measured as a function of time were used in calculating the K_La. Data collected during the first 20 s after start of

aeration were used. The increase in dissolved oxygen over time is described by the following equation:

$$\frac{dC_L}{dt} = K_L a(C_L^0 - C_L) \quad (1)$$

where C_L represents the dissolved oxygen concentration in the two-phase medium and C_L^0 represents the dissolved oxygen (or IPB) concentration in equilibrium with the gas phase. $K_L a$ represents total coefficient of mass transfer of gaseous substance:

Integration of Eq. 1 for $C_L = C_L^0$ at $t=0$, led:

$$\ln\left[\frac{(C_L^0 - C_L)}{C_L^0}\right] = -K_L a \bullet t \quad (2)$$

A plot of the left-hand side of Eq. 2 versus time was used to obtain the slope $-K_L a$. The $K_L a_{oxy}$ experiments were performed twice. For $K_L a_{IPB}$ measurements, the same procedure was applied without removing dissolved oxygen by sparging with nitrogen.

Bioreactor Configuration

A stirred bioreactor (LSL Biolafitte BL06.1, Saint Germain en Laye, France) containing a mixture (4.5 L) of oil and water was used; various ratios were tested. The temperature of the reactor was maintained at 25 °C. The air/IPB delivery system comprised a washing bottle containing 200 mL of IPB through which a fraction of the flow was blown. In order to evaluate the oxygen mass transfer coefficient as a function of hydrodynamic conditions, agitation speed was controlled between 300 and 900 rpm with an axial impeller (d=4.7 cm) and a four-blade Rushton turbine impeller (d=4.7 cm). Airflow was controlled between 1 and 6 L/min. In order to compare the mass transfer of IPB, the inlet concentration of IPB was maintained at 6 g/m^3 by continuously regulating a fraction of the total flow entering the wash bottle (total inlet flow—4.5 L/min). The experimental device (Fig. 1) allows the

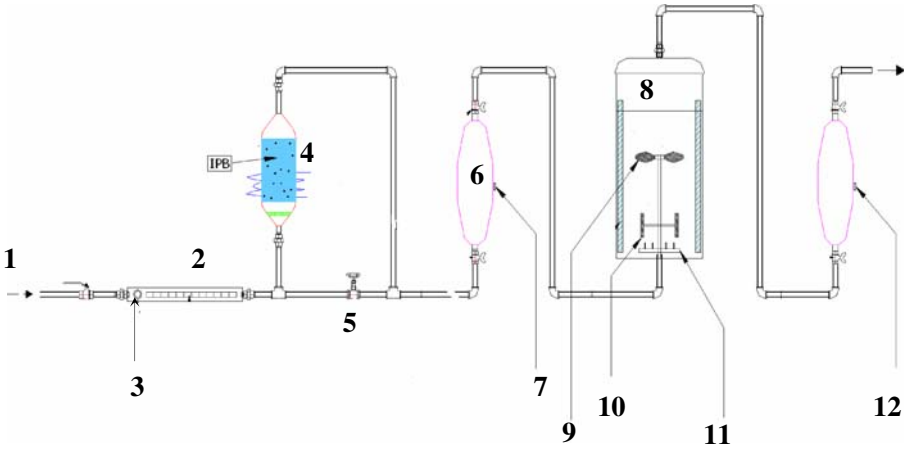

Fig. 1 Schematic of the experimental assembly. *1* Air inlet, *2* flow meter, *3* control valve, *4* bottle containing pollutant with a temperature control (*IPB*), *5* control valve to control the IPB concentration, *6* inlet sampling glass bulb (*glass with Teflon*), *7* septum (gas sampling), *8* stirred bioreactor, *9* helicoidal module, *10* TD4 module, *11* sparger, and *12* outlet sampling glass bulb (*glass with Teflon*)

generation of a gas effluent polluted with a fixed IPB concentration. The oxygen and IPB mass transfer occur in stirred bioreactor. Inlet and outlet gas sampling bubble allow quantification of IPB at the inlet and outlet of the bioreactor.

Chemicals

Isopropylbenzene was obtained from VWR (Leuven, Belgium). Silicone oils (polydimethylsiloxane under the trade name "200 fluid" and alkylaryl siloxane under the trade name "230 fluid") were obtained from Dow Corning (Seneffe, Belgium; Table 2).

Estimation of Isopropylbenzene

IPB composition of inlet gas and liquid samples have been analyzed by using a Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (FID). A 30-m HP.INNOWax column has been used with He as carrier gas at a column flow rate of 1 mL/min and a column head pressure of 50 kPa. The make-up gas flow rate of the FID is 30 mL/min for He, 30 mL/min for H_2, and 400 mL/min for air. IPB concentrations have been determined on the basis of the peak area compared to an IPB standard both for gaseous and liquids samples.

Sampling and Analysis

In order to determine the global coefficient of IPB mass transfer ($K_L a_{IPB}$; min^{-1}), homogeneous two-phase liquid samples are periodically withdrawn. The IPB concentration in both the liquid phases was estimated with a headspace sampling and injected as described above. $K_L a_{IPB}$ was determined by monitoring the IPB concentration into a two-phase liquid medium.

Medium

The two-phase liquid medium comprises various proportions of silicone oil with an aqueous phase having the following composition (M284): Tris-HCl 6.06 g/L, NaCl 4.68 g/L, KCl 1.49 g/L, NH_4Cl 1.07 g/L, Na_2SO_4 0.43 g/L, $MgCl_2 \cdot 6H_2O$ 0.20 g/L, Na_2HPO_4 $2H_2O$ 40 mg/L, $CaCl_2 \cdot 2H_2O$ 30 mg/L, Fe(III)NH_4 citrate 4.8 mg/L, $ZnSO_4 \cdot 7H_2O$ 0.144 mg/L, $MnCl_2 \cdot 4H_2O$ 0.1 mg/L, $H_3BO_3 \cdot 0.062$ mg/L, $CoCl_2 \cdot 6H_2O$ 0.19 mg/L, $CuCl_2 \cdot 2H_2O$ 0.017 mg/L, $NiCl_2 \cdot 6H_2O$ 0.024 mg/L, and $Na_2MoO_4 \cdot 2H_2O$ 0.036 mg/L. pH was set to 7.

Table 2 Physicochemical characteristics of each silicone oil tested.

Silicone oils	M_w (estimated; g/mol)	Boiling range (°C—0.5 mm Hg)	Flash point (°C)	Specific gravity	Surface tension (mN/m)
200 fluid (10 cSt)	1,250	>200 °C	211	0.935	20.1
200 fluid (100 cSt)	5,970	>200 °C	>326	0.964	20.9
200 fluid (350 cSt)	13,000	>200 °C	>326	0.96	21.1
230 fluid (1,300 cSt)			214	1.000–1.012	

Gas holdup

Gas holdup (ε) has been determined by measuring the liquid level variations in the reactor as a function of the various specific hydrodynamic conditions (agitation speed and airflow) and has been calculated using Eq. 3.

$$\varepsilon = 100 \times \frac{H - H_0}{H_0} \tag{3}$$

where H_0 and H are, respectively, the initial level of liquid in the reactor and the liquid level for different hydrodynamic conditions. All the experiments were performed twice.

Evaluation of the Effect of Silicone Oil Type on Oxygen and Pollutant Mass Transfer

According to the two-film theory, the transfer rate of gaseous substance from the gas phase to the liquid phase may be represented by Eq. 1 described above.

Results

The effect of the proportion of silicone oil and their viscosity were observed. In addition, the effect of hydrodynamic conditions on two parameters was evaluated: the oxygen mass transfer coefficient of ($K_L a$) and the gas holdup.

Effect of Silicone Oil and Hydrodynamical Conditions on the $K_L a$ of Oxygen

$K_L a$ of oxygen was estimated for three levels of airflow and three levels of agitation speed in order to estimate the influence of hydrodynamical conditions. Figure 2 shows the results obtained for different proportions of the silicone oil 200 fluid® (300 cSt).

Figure 2 shows that $K_L a$ of oxygen strongly decreases when the proportion of silicone oil increases. This reduction in oxygen mass transfer could be explained by the decrease of oxygen diffusion through oil droplets partially occupying the liquid film around bubbles or by the decrease of the interfacial area (a) [20]. According to MacMillan and Wang [22], this mechanism of flux reduction can only be applied to high viscosity oils; for example, *n*-paraffin has a lower oxygen permeability than water.

The positive impact of agitation speed and gas flow on oxygen mass transfer was also observed in the presence of silicone oil, although their impact was somewhat reduced at higher silicone oil content. Table 3 shows the slopes of the regression curves for $K_L a$ versus agitation speed and $K_L a$ versus gas flow rate. These results reveal that, at a higher silicone oil fraction, an increase of agitation speed or gas flow rate has lower impact on the oxygen mass transfer coefficient.

Moreover, an increase in the silicone oil content limits the influence of the two above-mentioned parameters. Thus, when the silicone oil fraction increases, an increase in agitation speed or gas flow does not permit to strongly increase the $K_L a_{oxy.}$

Effect of Silicone Oil on Gas Holdup

In biological treatment with a TPPB, it is important to ensure a sufficiently high gas holdup in order to improve mass transfer of both the oxygen and pollutants. Figure 3 shows the

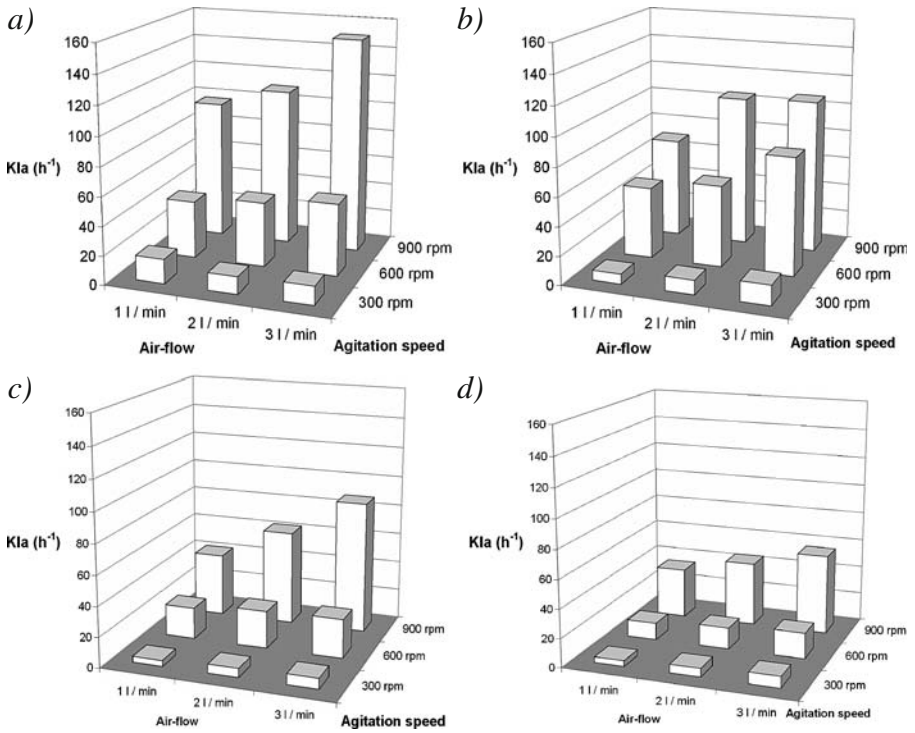

Fig. 2 Evolution of $K_L a_{O2}$ as a function of airflow and agitation speed **a** in M284 medium, **b** in two-phase medium with 10% 200 fluid® (300 cSt), **c** in two-phase medium with 30% 200 fluid® (300 cSt), and **d** in two-phase medium with 50% 200 fluid® (300 cSt). Standard deviations (n=2; not depicted) fluctuate between 1 and 6 h^{-1} for the set of experiment

evolution of gas holdup in TPPB as a function of the agitation speed and the gas flow rate at different fractions of silicone oil 200 fluid (300 cSt).

The results show that the addition of silicone oil allows to reach a higher gas holdup rate in the two-phase medium. In the absence of silicone oil, the gas holdup did not exceed 5% of the initial volume. However, an addition of only 10% of silicone oil allows for the increase of the gas holdup to approximately 12% at the highest airflow rate, leading to a twofold increase in the gaseous phase retention time. Another interesting aspect is that the gas holdup was highly dependent on the airflow in the presence of silicone oil in aqueous medium. Thus, retention time of the gaseous phase into the reactor did not decrease in the same proportion as the airflow increase. Indeed,

Table 3 Influence of agitation speed and gas flow on the $K_L a$ of oxygen according to the proportion of silicone oil.

	Slopes of the regression curves agitation speed versus $K_L a_{oxy}$ (h^{-1} rpm^{-1})	Slopes of the regression curves gas flow versus $K_L a_{oxy}$ of oxygen (L^{-1})
M284	0.1185	10.955
10% silicone oil	0.1036	13.776
30% silicone oil	0.0769	8.750
50% silicone oil	0.0555	5.77

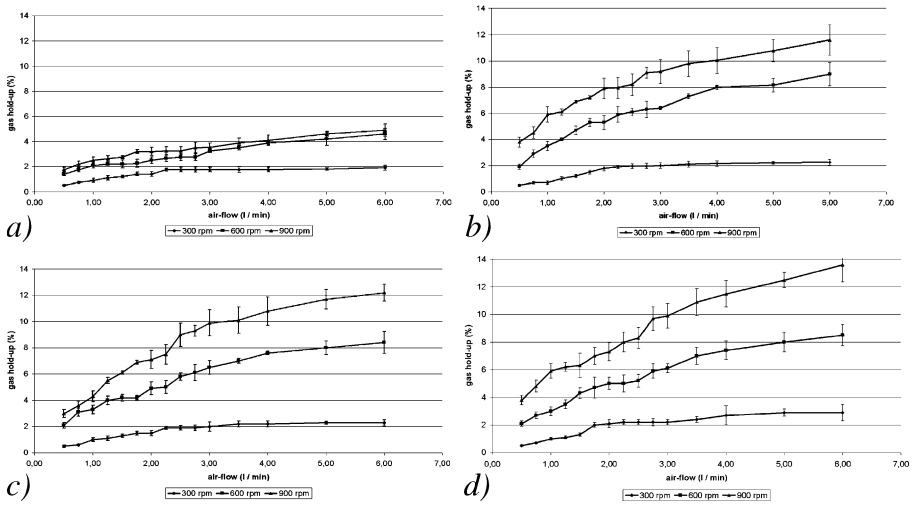

Fig. 3 Gas holdup as a function of airflow and agitation speed **a** in M284 medium, **b** M284 medium with 10% silicone oil, **c** M284 medium with 30% silicone oil, and **d** M284 medium with 50% silicone oil

silicone oil has reduced the establishment of the holdup steady state the increase in airflow compared to the water medium (M284). However, adding 30% and 50% silicone oil did not allow to further increase the gas holdup.

In the presence of silicone oil, the gas holdup has reached a stationary value at a higher airflow. Nevertheless, agitation speed has a synergistic effect with the silicone oil on the gas holdup. A slow agitation speed did not allow reaching higher gas holdup. Combination of high agitation speed (more than 600 rpm) with the addition of silicone oil delayed the establishment of the holdup steady state as a function of airflow rate.

The results further demonstrate the synergistic effect of the addition of 10% of silicone oil, with agitation corresponding to a peripheral speed of 1.5 m/s. The effect of oil addition on gas–liquid interfacial area, a, has been studied in the past. It has been observed that small droplets of organic phase could result in reduced rates of gas-bubble coalescence and thus in increased gas–liquid interfacial (a) area [23]. Rols et al. [24] concluded that the mean diameter of the bubble decreased by 15% and the gas–liquid interfacial area increased proportionally in the presence of emulsified oxygen vector.

The gas–liquid interfacial area (a) thus probably increases with the addition of silicone oil since a can be estimated by the following formulae, $6\varepsilon/d_b$ (where ε is gas holdup and d_b the bubble diameter). On the basis of this assumption, it can be concluded that the reduction of $K_L a_{oxy}$ in two-phase medium with silicone oil was not due to a reduction of interfacial area but due to the reduction of K_L.

Effect of the Type of Silicone Oil on the Gas Transfer

It has been shown that this was beneficial for the gas holdup and this condition was thus used for further analysis. Polydimethylsiloxane of various viscosities have been compared with an alkylarylsiloxane fluid. It has been hypothesized that the increased “hydrophobic” behavior of the later can have a positive effect on the transfer mass by increasing the solubility of the pollutant in the siloxane phase.

Oxygen Mass Transfer

Table 4 presents the equilibrium concentration of dissolved oxygen in water, M284, and various two-phase media with silicone oil (10% in M284) at 25 °C after oxygen saturation in aerated stirred medium. The oxygen solubility slightly increases when silicone oil is added to the M284 medium. It allows a small increase of the driving force term $\left(C_{\mathrm{L}}^{0} - C_{\mathrm{L}}\right)$ during aeration to compensate in part for the observed reduction of $K_{\mathrm{L}}a$. The highest oxygen equilibrium concentration has been measured for the low-viscosity silicone oil (10 cSt). Silicone oil addition did not allow for significant improvement of oxygen mass transfer but oxygen solubility is not affected. Figure 4 shows the evolution of the global oxygen mass transfer coefficient ($K_{\mathrm{L}}a$) into the bioreactor for various types and proportions of silicone oil. It clearly indicates that the experimental values of $K_{\mathrm{L}}a$ depend on the silicone oil fraction in the system. More specifically, for the three 200 fluid silicone oil tested, the value of $K_{\mathrm{L}}a$ decreased when their proportion increased. However, the evolution of $K_{\mathrm{L}}a$ is inverted when 230 fluid silicone oil is added. Absolute values in this last case remained lower than for other silicone oils, which could be explained by the higher viscosity of the 230 fluid (1,300 cSt.) It is obvious that an increase in the oil viscosity leads to a decrease of $K_{\mathrm{L}}a$. Adding 10% silicone oil (10 cSt) led to a $K_{\mathrm{L}}a$ value (116 h^{-1}) close to the one observed in M284 medium (150 h^{-1}). The use of low viscosity silicone oil allows obtaining an oxygen mass transfer rate that is sufficiently high because of an oxygen solubility slightly higher than in M284 (C_{L}^{0}, 8.9 versus 8.1 mg O_2/L; see Table 4).

Isopropylbenzene Mass Transfer

Isopropylbenzene has been chosen as representative for monoaromatic compounds and is generally considered as poorly water soluble (0.074 g/L at 20 °C and a "w/o" ratio of 0.000218) [25]. By contrast, IPB is readily miscible in the different silicone oils selected. The apparent maximum solubility $\left(C_{\mathrm{L\,IPB}}^{0}\right)$ has thus been defined as the IPB concentration at equilibrium when the quantity absorbed equals the quantity volatilized due to the air stripping. We have thus named this concentration $\left(C_{\mathrm{L}}^{0}\right)$ in two-phase medium as apparent solubility of IPB (Table 5).

The apparent solubility of IPB into two-phase media considerably increases at higher fractions of silicone oil. The oil viscosity has apparently little impact on this solubility. Compared with the other silicone oils, addition of 230 fluid® showed lower impact on IPB solubility, making it less attractive for this study. The use of silicone oil allows to increase the driving force term $\left(C_{\mathrm{L}}^{0} - C_{\mathrm{L}}\right)$ during the IPB transfer from the gaseous phase to the aqueous phase. The IPB mass transfer in TPPB was studied at an airflow rate of 3 L/min and an IPB concentration in the gaseous effluent maintained at 6 g/m^3. Determination of the

Table 4 Equilibrium concentration of oxygen $\left(C_{\mathrm{L\,oxy}}^{0}\right)$ into two-phase media with 10% of various silicone oils.

Medium	Equilibrium concentration $\left(C_{\mathrm{L\,oxy}}^{0}\right)$ [mg O_2/L]
Water	7.8
M284	8.1
Silicone oil 200 fluid (10 cSt)	8.9
Silicone oil 200 fluid (100 cSt)	8.8
Silicone oil 200 fluid (300 cSt)	8.7
Silicone oil 230 fluid	8.4

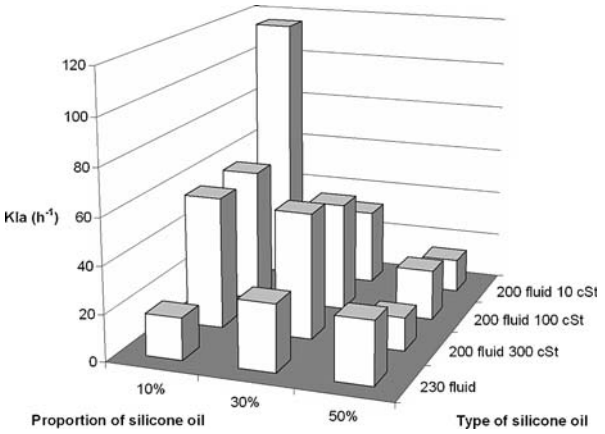

Fig. 4 Evolution of $K_L a_{oxygen}$ as a function of type and fraction of silicone oil in two-phase medium with an agitation speed of 600 rpm and an airflow of 3 L/min. Standard deviations (n=2; not depicted) fluctuate between 2 and 8 h^{-1} for the set of experiments

global coefficient of IPB mass transfer ($K_L a_{IPB}$) has been done by measuring the global IPB concentration in the two-phase medium. Figure 5 presents the results obtained for the four studied oils at various proportions of oil (10%, 30%, and 50%).

Results clearly indicate an influence of the viscosity and oil content on the IPB global coefficient mass transfer ($K_L a_{IPB}$). Use of low viscosity oil has made it possible to increase this coefficient. In fact, the evolution of IPB mass transfer as a function of silicone oil type and content is similar to those obtained with oxygen. Above 10% silicone oil, both mass transfer coefficients were strongly reduced, probably due to the increase in two-phase medium viscosity, which was described by Dumont and Delmas [20].

Discussion

Most of the studies devoted to the understanding of gas transfers in the presence of an organic phase have focused their attention on oxygen and its improvement. Only a few studies consider the mass transfer of pollutants in a two-phase partitioning bioreactor. In this work, both the IPB and oxygen mass transfer were considered.

Considering the oxygen mass transfer, the results of the present study are similar to the experimental values of $K_L a$ obtained by Nielsen et al. [26] at various operating conditions and "organic" phase proportion, the two studies have shown a reduction of $K_L a$ at higher organic phase proportions. Dumont et al. [27] have shown that addition of silicone oils hinders oxygen mass transfer compared to air/water systems. Nevertheless, the results have shown an interesting synergistic effect between an oil fraction of 10% and a peripheral speed of 1.5 m/s leading to $K_L a$ values similar to those observed for an aqueous medium. Global oxygen mass

Table 5 Apparent solubility of IPB $\left(C^0_{L\,IPB}\right)$ into various two-phase medium—(mg/L of two-phase media).

Proportion of silicone oil (%)	230 fluid	200 fluid (10 cSt)	200 fluid (100 cSt)	200 fluid (300 cSt)
10	3,455	29,100	26,500	27,500
30	25,200	58,500	58,400	64,000
50	47,000	74,300	74,500	81,000

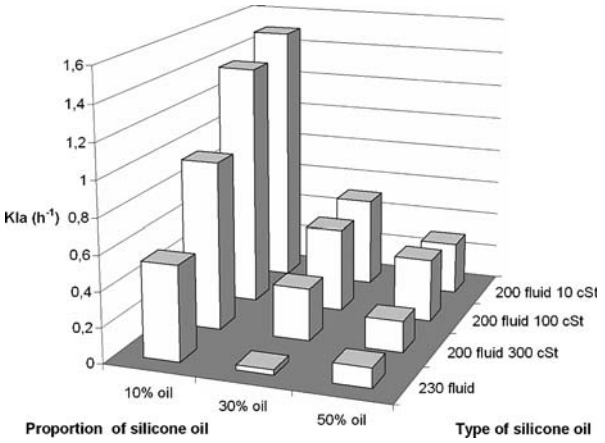

Fig. 5 Evolution of $K_L a_{IPB}$ as a function of the type and fraction of silicone oil in two-phase medium with an agitation speed of 600 rpm and an airflow of 3 L/min

transfer can be improved by adding a proportion of 10% silicone oil (10 cSt.) since oxygen solubility reaches 8.89 mg O_2/L versus 8.13 mg O_2/l in M284 medium. Thus, the combination of good $K_L a$ values and oxygen solubility led to a better oxygen mass transfer.

Considering the IPB mass transfer, it has been clearly shown that silicone oil did not increase the $K_L a$ of this monoaromatic pollutant. However, the IPB apparent maximum solubility in a two-phase medium allowed a better mass transfer because it was related to a strong increase in the driving force term $\left(C_L^0 - C_L\right)$. The theoretical maximal transfer rate calculated from results for the various media studied are shown in Table 6 (g IPB transferred/m^3_{react} h). It can be noted that the IPB transfer rate is not calculated for aqueous M284 media since water is too quickly saturated with IPB because of its very poor water solubility.

The best calculated transfer rate (43,600 g/m^3_{react} h) was obtained by using a proportion of 10% 200 fluid (10 cSt) in the two-phase media. Further addition of polydimethylsiloxane led to a reduction in the theoretical maximal transfer rate. The viscosity of the oil phase appeared to be the most critical parameter governing the IPB mass transfer.

These results agree with the model of transfer described by Marcelis et al. [28] for dibenzothiophene mass transfer in oil/water dispersion, where density and interfacial tension were found to be of minor importance. The results obtained have highlighted the interest of two-phase partitioning bioreactor in the context of biological off-gas treatment. Conventional techniques such as biofilters have shown limited elimination capacities for hydrophobic compounds because of a poor mass transfer from the gas to the aqueous phase [4]. Two-phase partitioning bioreactors could be a cost-effective way of treating gases that contain high concentrations of hydrophobic compounds for which the traditional biological techniques present some limits.

Table 6 Theoretical maximal transfer rate of IPB for various media.

Type of silicone oil	10% silicone oil $\left(g/m^3_{react}\ h\right)$	30% silicone oil $\left(g/m^3_{react}\ h\right)$	50% silicone oil $\left(g/m^3_{react}\ h\right)$
230 fluid	1,900	700	5,400
200 fluid (10 cSt)	43,600	29,800	22,300
200 fluid (100 cSt)	36,500	28,000	28,800
200 fluid (300 cSt)	26,400	19,200	14,500

Clearly, the second phase may still have some ability to buffer the transfer pollutants against the gaseous phase in the silicone oil on pollution peaks. Silicone oil can be regarded as an organic phase reservoir for the toxic substrates since the substrate concentration in the biotic phase can be maintained below the inhibitory level. The partition process itself is controlled by the mass transfer from organic to aqueous phase and afterwards by the subsequent metabolic activity of microorganisms.

In this study, the power input required was estimated at 220 W/m^3 (according to [29]), a much lower value than the one reported by Nielsen et al. [26] (between 1,000 and 5,000 W/m^3). These energy requirements are acceptable from the viewpoint of a scaling up.

Maximal calculated IPB transfer rate (200 fluid (10 cSt); 10%) strongly exceed the elimination capacities of TPPB mentioned in the literature (except for 230 fluid silicone oil). It can thus be proposed to work with a smaller proportion of silicone oil (below 10%) as the second phase in the TPPB since it does not improve the oxygen mass transfer. The use of very low viscosity silicone oil (<5 cSt) could be also considered but their "flash point" strongly decreases with lowering of viscosity, which involves safety consideration.

Conclusion

This study has contributed to a better understanding of transfer phenomenon in two-phase media. It demonstrated the synergistic effect of silicone oil addition and hydrodynamical conditions on the global mass transfer coefficient of oxygen and gas holdup.

The $K_L a_{oxy}$ being kept almost similar compared to aqueous media (M284); the small increase in oxygen solubility in two-phase media (10%) induces acceptable oxygen transfer rates in two-phase media in spite of the oil-induced oxygen transfer resistance. Increase in proportion of silicone oil induces a reduction in $K_L a_{oxy}$ but an increase in gas holdup; it can also been suggested that adding the silicone oil causes a decrease in K_L, which is not compensated by a similar increase in a. However, future studies should include measurement of bubble diameter (d_b) to verify that the increase in the proportion of silicone oil does not cause an increase in them in water/silicone oil media.

This work has also focused on mass transfer of pollutant from gaseous phase to two-phase medium. Adding silicone oil strongly increases the driving force term $\left(C_L^0 - C_L\right)$, especially for high fraction of low viscosity silicone oil. However, it does not seem useful to exceed a volume fraction of 10% of silicone oil since $K_L a_{IPB}$ strongly decreases at higher silicone oil fraction. In addition, theoretical maximal transfer rates calculated for IPB suggest that smaller proportions of silicone oil could be considered to treat gaseous effluents. Lastly, the transfer capacities of such bioreactor confirm their potentialities in the framework of gaseous treatment, especially for highly concentrated effluents that are not treatable by the traditional biofilters because the transfer from gaseous phase to aqueous phase is too low.

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