



VOC absorption in a countercurrent packed-bed column using water/silicone oil mixtures: Influence of silicone oil volume fraction

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ABSTRACT

A calculation procedure to determine the influence of the silicone volume fraction on the physical absorption of VOCs in water/silicone oil mixtures is presented ($\eta_{\text{silicone oil}} = 5 \text{ mPa s}$). It is based on the “equivalent absorption capacity” concept previously developed by Dumont et al. (2010) [1] and applied to a countercurrent gas–liquid absorber. The calculation procedure is first applied to three VOCs: dimethylsulphide (DMS), dimethyldisulphide (DMDS) and toluene, and then generalised to other VOCs. The influence of VOC partition coefficients ($H_{\text{voc,water}}$ and $H_{\text{voc,solvent}}$) and the ratio $m_R = H_{\text{voc,water}}/H_{\text{voc,solvent}}$ is shown. For VOCs having a much higher affinity for silicone oil than for water ($m_R > 20$ as for DMDS and toluene), it is preferable to use pure silicone oil rather than water/silicone oil mixtures for absorption.

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1. Introduction

The biological treatment of air loaded with hydrophobic Volatile Organic Compounds (VOCs) can be enhanced by the addition of an organic solvent whose affinity for these pollutants must be substantially higher than that for water. The treatment can be achieved in a bioscrubber in which the pollutants are first scrubbed into the liquid phase (the solvent) before being introduced into a two-phase partitioning bioreactor (TPPB). VOCs are then transferred from the solvent to the aqueous phase in order to be degraded by microorganisms and the regenerated solvent is recirculated back to the absorber. At the laboratory scale, TPPB has been demonstrated to be effective at degrading a variety of toxic substrates [2]. One of the most important parameters of this biological treatment is the selection of an appropriate solvent. It is commonly known that the solvent must be biocompatible, non-biodegradable, non-toxic, inexpensive and have a high affinity (partition coefficient) for pollutants as well as low volatility and viscosity. Many studies devoted to a systematic solvent selection strategy are available in the literature ([3–5] among others). Recently, silicone oils have been identified

as good products for such applications [6]. However, they are relatively expensive (around 26 €/kg for a silicone oil with a dynamic viscosity equal to 5 mPa s when purchased in a 190 kg barrel). Consequently, one of the challenges of this process is to minimise the amount necessary for the mass transfer of pollutants. In other words, for a solvent having a high affinity for pollutants, it might be wiser to feed the gas–liquid absorber with a water/silicone oil mixture at low silicone oil volume fraction rather than with pure solvent. From a mass transfer point of view, it has been established that the absorption performance depends on the type and the percentage of the solvent [7,8] with an optimal percentage of solvent situated around 10% [9–11]. The occurrence of such an optimal percentage can be explained by the fluid properties of the solvent (mainly surface tension and dynamic viscosity). However, in order to design the absorption column satisfactorily, the silicone oil volume fraction must be judiciously determined to limit the capital costs. The aim of this paper is to present a calculation procedure to determine the silicone oil quantity needed for the mass transfer of VOCs according to the silicone oil volume fraction. This calculation procedure, applied to a countercurrent gas–liquid absorber, is derived from the “equivalent absorption capacity” concept developed by Dumont et al. [1] based on the experimental absorption of three VOCs: dimethylsulphide (DMS), dimethyldisulphide (DMDS) and toluene. Two cases are considered in this study:

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Nomenclature

<i>A</i>	absorption factor
<i>E</i>	efficiency (-)
<i>G</i>	gas flow rate (mol h ⁻¹)
<i>H</i>	partition coefficient (Pa m ³ mol ⁻¹)
<i>L</i>	liquid flow rate (mol h ⁻¹)
<i>M</i>	molecular weight (kg mol ⁻¹)
<i>m</i>	slope of the equilibrium line (-)
<i>m_R</i>	distribution coefficient (-)
<i>n</i>	number of stages (-)
<i>R</i>	ideal gas constant (8.314 J mol ⁻¹ K ⁻¹)
<i>T</i>	temperature (K)
<i>V_G</i>	gas flow rate (m ³ h ⁻¹)
<i>V_L</i>	liquid mixture flow rate (m ³ h ⁻¹)
<i>V_{solvent}</i>	silicone oil flow rate (m ³ h ⁻¹); <i>V_{solvent}</i> = ϕV_L
<i>x</i>	molar fraction of VOC in the liquid phase (-)
<i>y</i>	molar fraction of VOC in the gas phase (-)

Greek letters

ϕ	silicone oil volume fraction (-)
η	dynamic viscosity (Pa s)
ρ	density (kg m ⁻³)

Superscripts

*	equilibrium
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Subscripts

0	bottom of the column
G	gas phase
L	liquid phase
max	maximum
min	minimum
mixture	water/silicone oil mixture
solvent	relative to silicone oil
VOC	Volatile Organic Compound
water	water
z	top of the column

Table 1

Physical properties of the three pollutants (*T* = 298 K; partition coefficients in Pa m³ mol⁻¹).

	DMDS	DMS	Toluene
Molecular weight (g mol ⁻¹)	94.2	62.1	92.1
Density (kg m ⁻³)	1046	850	870
Partition coefficient in water (<i>H_{voc,water}</i>)	111.9	182.1	680
Partition coefficient in silicone oil (<i>H_{voc,solvent}</i>)	3.4	17.7	2.3
Ratio <i>m_R</i> = <i>H_{voc,water}</i> / <i>H_{voc,solvent}</i>	33	10	296

tal data, it has been established that material balances in both molar and volume units could be satisfied only if the absorption capacity of a unit volume of water/silicone oil mixture is equivalent to the absorption capacity of the same volume of a homogeneous phase whose physical properties (partition coefficient *H_{voc,mixture}*, density $\rho_{mixture}$, and molecular weight *M_{mixture}*) can be expressed as a function of the silicone oil volume fraction ϕ (Eqs. (1)–(3)). As it can be observed in Eq. (3), *M_{mixture}* is logically based on the molecular weights of water and silicone oil through $(1 - \phi)M_{water}$ and $\phi M_{solvent}$, respectively, but their relative importance is corrected using the “equivalent absorption coefficients” *H_{voc,mixture}*/*H_{voc,water}* and *H_{voc,mixture}*/*H_{voc,solvent}*. Indeed, as demonstrated in [1], the “equivalent absorption coefficients” must be used in order to take into account the actual absorption capacities of the mole numbers of water and silicone oil, respectively. To satisfy the material balance, the importance of the mole number of water participating to the absorption must be moderated using a correction factor (*H_{voc,mixture}*/*H_{voc,water}*) while the importance of the mole number of silicone oil must be adapted using the factor (*H_{voc,mixture}*/*H_{voc,solvent}*). As explained in [1], the “equivalent absorption coefficients” must also be used to express the equivalent density of the pseudo-homogeneous phase (Eq. (2)) in order to satisfactorily fit experimental results. Without the slight corrections ($\rho_{mixture}/\rho_{water}$ and $\rho_{mixture}/\rho_{solvent}$) applied to balance the importance of water and silicone oil in the calculation of the molecular weight *M_{mixture}*, Eq. (3) could lead to *M_{mixture}* values higher than *M_{solvent}* for some values of ϕ .

$$\frac{1}{H_{voc,mixture}} = \frac{1 - \phi}{H_{voc,water}} + \frac{\phi}{H_{voc,solvent}} \quad (1)$$

$$\rho_{mixture} = (1 - \phi)\rho_{water} \frac{H_{voc,mixture}}{H_{voc,water}} + \phi\rho_{solvent} \frac{H_{voc,mixture}}{H_{voc,solvent}} \quad (2)$$

$$M_{mixture} = (1 - \phi)M_{water} \frac{H_{voc,mixture}}{H_{voc,water}} \frac{\rho_{mixture}}{\rho_{water}} + \phi M_{solvent} \frac{H_{voc,mixture}}{H_{voc,solvent}} \frac{\rho_{mixture}}{\rho_{solvent}} \quad (3)$$

In an absorption process, it is convenient to define an absorption factor *A* as follows:

$$A = \frac{L}{mG} \quad (4)$$

The absorption factor *A* corresponds to the ratio of the slope of the operating line *L/G* to that of the equilibrium line *m* (Fig. 1). *A* is constant when both lines are straight, which is the case for air treatment applications. The relationship between *m* and the partition coefficient is given by Eq. (5).

$$m = H_{voc,mixture} \left(\frac{1}{RT} \right) \left(\frac{M_G \rho_{mixture}}{M_{mixture} \rho_G} \right) \quad (5)$$

The liquid mole flow rate (*L* = *L_{mixture}*) is expressed by Eq. (6):

$$L_{mixture} = V_L \frac{\rho_{mixture}}{M_{mixture}} \quad (6)$$

For a given gas flow rate to be treated, and assuming that it remains unchanged during absorption, a combination of Eqs. (4)–(6) gives

- Gas and liquid flow rates are known. They remain unchanged whatever the silicone oil volume fraction. What are the results on the absorption factor and on the number of ideal stages?
- The gas flow rate to be treated is given and the absorption factor is chosen. How much liquid flow rate is needed to achieve the absorption satisfactorily as a function of the silicone oil volume fraction?

2. Solvent and VOCs

In this study, the calculation is based on the use of silicone oil (polydimethylsiloxane), Rhodorsil® fluids 47V5 from the Rhodia Company, France. The physical properties of this oil are: viscosity: 5 mPa s; density: 930 kg m⁻³; molecular weight: 740 g mol⁻¹.

The physical properties of the three VOCs are summarised in Table 1. The determination of the partition coefficients is presented in Dumont et al. [1]. The ratio *m_R* is the distribution coefficient of VOCs between the aqueous and silicone oil phases.

3. “Equivalent absorption capacity” concept

This empirical concept, presented in a previous paper [1], was developed from the physical absorption measurements of DMS, DMDS and toluene in water/silicone oil mixtures varying in terms of silicone oil volume fraction. From these experimen-

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