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

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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.

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> = <i>φV_L</i>
<i>x</i>	molar fraction of VOC in the liquid phase (-)
<i>y</i>	molar fraction of VOC in the gas phase (-)

Greek letters

<i>φ</i>	silicone oil volume fraction (-)
<i>η</i>	dynamic viscosity (Pa s)
<i>ρ</i>	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 *ρ_{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 $(1 - \phi)M_{\text{water}}$ and ϕM_{solvent} , respectively, but their relative importance is corrected using the “equivalent absorption coefficients” $H_{\text{voc,mixture}}/H_{\text{voc,water}}$ and $H_{\text{voc,mixture}}/H_{\text{voc,solvent}}$. 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 ($H_{\text{voc,mixture}}/H_{\text{voc,water}}$) while the importance of the mole number of silicone oil must be adapted using the factor ($H_{\text{voc,mixture}}/H_{\text{voc,solvent}}$). 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 ($\rho_{\text{mixture}}/\rho_{\text{water}}$ and $\rho_{\text{mixture}}/\rho_{\text{solvent}}$) 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*.

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

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

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

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).

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

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

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

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-

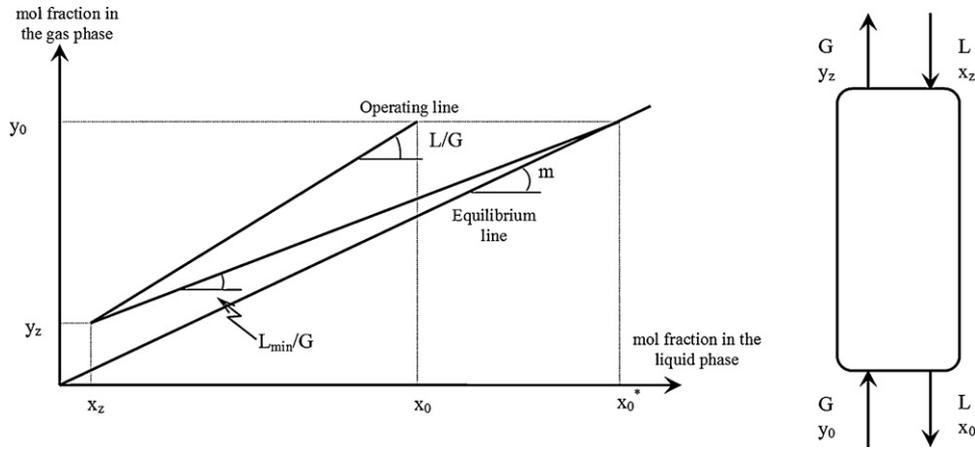


Fig. 1. Material-balance diagram for a countercurrent absorption column.

an expression of the absorption factor versus ϕ (Eq. (7); see Appendix A). From this relationship, it is possible to calculate the amount of water/silicone oil mixture (V_L) needed for the mass transfer of the three considered VOCs.

$$A = \frac{L_{\text{mixture}}}{mG} = \frac{V_L}{V_G} \frac{RT}{H_{\text{voc,mixture}}} \quad (7)$$

Replacing the expression of $H_{\text{voc,mixture}}$ (Eq. (1)) in Eq. (7) gives:

$$A = \frac{V_L}{V_G} RT \left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{V_L}{V_G} RT \frac{1}{H_{\text{voc,water}}} \quad (8)$$

4. VOC absorption for a given liquid flow rate V_L . Influence of the silicone oil volume fraction on the absorption efficiency

It is assumed that the countercurrent absorption column is able to contact a given gas flow rate ($V_G = 10,000 \text{ m}^3 \text{ h}^{-1}$) with a given liquid flow rate ($V_L = 100 \text{ m}^3 \text{ h}^{-1}$; the liquid flow rate remaining constant whatever the silicone oil volume fraction in the mixture). In such conditions and according to Eq. (8), the absorption factor is a linear function of ϕ . Using the Kremser–Souders–Brown equation (Eq. (9) [12]), the VOC absorption efficiency can be deduced for each ϕ value and according to the number of stages (Fig. 2).

$$E = \frac{A^{n+1} - A}{A^{n+1} - 1} \quad (9)$$

From Fig. 2 and Eq. (8), it can be concluded:

- (i) As the reciprocal of $H_{\text{voc,water}}$ is relatively small compared to $1/H_{\text{voc,solvent}}$, it appears that the slope of the absorption factor is governed by the $H_{\text{voc,solvent}}$ value. In other words, the $H_{\text{voc,solvent}}$ value represents the most influential parameter on absorption; more influential than the ratio of the partition coefficients. As observed in Fig. 2, DMDS and toluene present similar absorption behaviour due to their close $H_{\text{voc,solvent}}$ values (3.4 and $2.3 \text{ Pa m}^3 \text{ mol}^{-1}$, respectively) whereas the absorption of DMS is limited in relation to its partition coefficient for silicone oil ($17.7 \text{ Pa m}^3 \text{ mol}^{-1}$; Table 1).
- (ii) For DMDS and toluene, absorption efficiencies higher than 90% are achieved for silicone oil volume fractions ranging from 10 to 20% according to the number of stages. In this case, the absorption factor is around 1.5 indicating that these conditions will be useful for air treatment. For DMS, such conditions will be reached only when using pure silicone oil and requiring a large number of stages.

5. VOC absorption for a given absorption factor ($A = 1.5$). Influence of the silicone oil volume fraction on the liquid flow rate

Most frequently in absorber calculations, the values of the gas flow rate and the VOC concentration entering the column are given, while the liquid flow rate must be calculated. For a countercurrent packed-bed column, the highest attainable VOC concentration in the liquid is equal to the concentration which is in equilibrium with the gas entering the column (Fig. 1). Hence, the lowest value of the liquid flow rate is:

$$\frac{L_{\text{min}}}{G} = \frac{y_0 - y_z}{x_0^* - x_z} \quad (10)$$

In the specific case of biological treatment of VOCs, it can be reasonably assumed that the liquid mixture entering the column has been regenerated and consequently $x_z \neq 0$. Moreover, the gaseous concentration at the column outlet is required to be close to zero ($y_z \neq 0$). Hence, Eq. (10) becomes:

$$\frac{L_{\text{min}}}{G} = \frac{y_0}{x_0^*} \quad (11)$$

As $y_0 = mx_0^*$, the minimum liquid flow rate is then:

$$L_{\text{min}} = mG \quad (12)$$

As the L/G ratio is important in the economics of absorption in a countercurrent column, the liquid flow rate for the absorber is generally between 1.1 and 1.5 times the minimum rate [13]. Consequently, the absorption factor A must range from 1.1 to 1.5. In this study, A has been chosen to be equal to 1.5. The minimum quantity of the water/silicone oil mixture needed for absorption is then calculated from Eq. (7) for a gas flow rate equal to $10,000 \text{ m}^3 \text{ h}^{-1}$. As observed in Fig. 3, the liquid flow rates of the mixture are logically related to the partition coefficients of the VOC in water and silicone oil, respectively. For toluene, the liquid flow rate drops from $4116 \text{ m}^3 \text{ h}^{-1}$ corresponding to water alone ($\phi = 0$) to $14 \text{ m}^3 \text{ h}^{-1}$ for silicone oil alone ($\phi = 1$). The liquid flow rate drops from 677 to $21 \text{ m}^3 \text{ h}^{-1}$ and from 1100 to $107 \text{ m}^3 \text{ h}^{-1}$ for DMDS and DMS, respectively. As expected, the ratio of the liquid flow rates $V_{\text{water}(\phi=0)}/V_{\text{solvent}(\phi=1)}$ corresponds to the ratio $m_R = H_{\text{voc,water}}/H_{\text{voc,solvent}}$ presented in Table 1. As silicone oil is relatively expensive (around 26 €/kg for the purchase of a 190 kg barrel), the optimum silicone oil amount must be found by balancing the operating costs for absorption against the fixed costs of the equipment. For each silicone oil volume fraction, it is possible to calculate the silicone oil amount in the mixture ($V_{\text{solvent}(\phi)} = \phi V_L$) and to compare it with the maximum quantity of silicone oil needed for

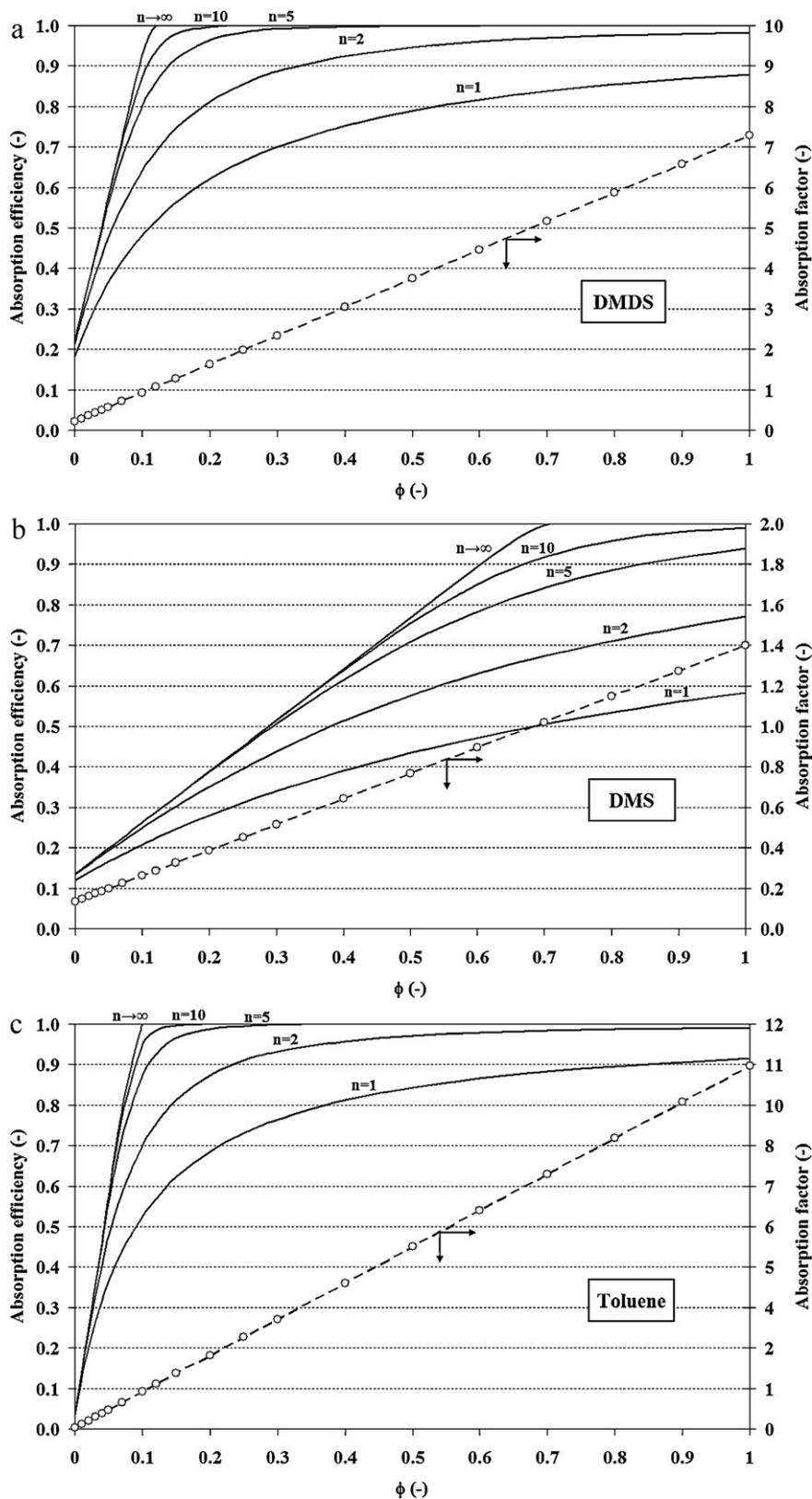


Fig. 2. Absorption efficiency (solid lines) and absorption factor (A) (dashed line) versus silicone oil volume fraction for a countercurrent absorption column ($V_C = 10,000 \text{ m}^3/\text{h}$; $V_L = 100 \text{ m}^3/\text{h}$; $T = 298 \text{ K}$).

absorption corresponding to $\phi = 1$ ($V_{\text{solvent max}}$). The results are presented in Fig. 4. For a VOC having a much higher affinity for silicone oil than for water (DMDS and toluene), it appears that it is unwise to use a water/silicone oil mixture for absorption. For instance, if a

water/silicone oil mixture with only 10% of solvent (90/10, v/v) is chosen to absorb toluene, it will be necessary to use a quantity of silicone oil equal to 97% of the amount needed for an absorption in the pure solvent (in this case, $13.5 \text{ m}^3 \text{ h}^{-1}$ of silicone oil should

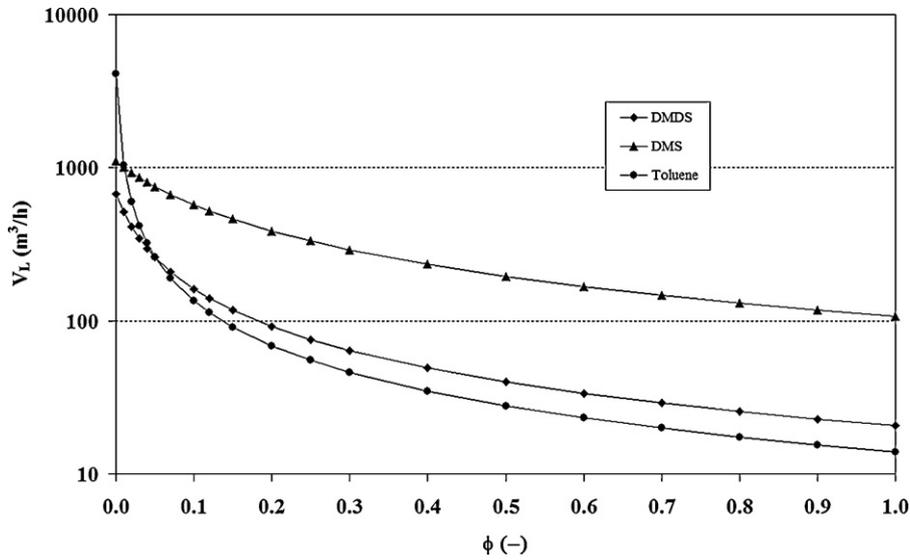


Fig. 3. Minimum flow rate of the water/silicone oil mixture needed for absorption versus silicone oil volume fraction ($V_G = 10,000 \text{ m}^3/\text{h}$; $A = 1.5$).

be used compared to $13.9 \text{ m}^3 \text{ h}^{-1}$ for an absorption in pure silicone oil). For DMDS absorption in a 90/10 (v/v) mixture, it will be necessary to use a quantity of silicone oil equal to 78.5% of the maximum amount of silicone oil (i.e. $16.2 \text{ m}^3 \text{ h}^{-1}$ compared to $20.6 \text{ m}^3 \text{ h}^{-1}$ for an absorption in pure silicone oil). Hence, from these examples, it can be concluded that the use of a mixture with a low silicone oil volume fraction (90/10, v/v) to absorb DMDS or toluene: (i) requires a quantity of solvent roughly equal to the amount needed for an absorption in a pure silicone oil and (ii) involves designing a column with a much larger diameter than that actually needed for an absorption in pure solvent. Consequently, the absorption should be carried out by contacting the polluted air with pure silicone oil. In this case, the column diameter will be as small as possible in order to limit the costs of the equipment.

Considering DMS absorption (VOC with the lowest $H_{\text{voc,water}}/H_{\text{voc,solvent}}$ ratio), it can be concluded from Fig. 4 that the use of a water/silicone oil mixture with only 10% of silicone oil requires $57.1 \text{ m}^3 \text{ h}^{-1}$ of silicone oil corresponding to 53.3% of the amount needed for an absorption in pure silicone oil ($107.2 \text{ m}^3 \text{ h}^{-1}$). In this case, a specific study should be carried out

to determine the diameter of the column which could be used to contact, on the one hand, the polluted air and the pure silicone oil ($107.2 \text{ m}^3 \text{ h}^{-1}$) and, on the other hand, the polluted air and the 90/10 (v/v) water/silicone oil mixture representing $57.1 \text{ m}^3 \text{ h}^{-1}$.

Assuming that the calculation procedure developed for the absorption of DMDS, DMS and toluene in water/silicone oil mixtures can be applied to the absorption of other VOCs satisfying Eq. (1) and characterised by their partition coefficients ($H_{\text{voc,water}}$ and $H_{\text{voc,solvent}}$), a mathematical development generalised to any VOC is presented hereafter. It is assumed that the VOC distribution coefficients (m_R) range from 1 to 1000.

The ratio $V_{\text{solvent}(\phi)}/V_{\text{solvent max}}$ is derived from Eq. (7) applied for both conditions: $0 < \phi < 1$ and $\phi = 1$ (see Appendix B).

$$\frac{V_{\text{solvent}(\phi)}}{V_{\text{solvent max}}} = \frac{1}{[1 + (1/m_R)((1/\phi) - 1)]} \quad (13)$$

According to Eq. (13), for a given silicone volume fraction ϕ , the ratio $V_{\text{solvent}(\phi)}/V_{\text{solvent max}}$ depends only on the ratio of VOC partition coefficients, m_R (Fig. 5). For $\phi = 0.1$, the results obtained for DMDS, DMS and toluene developed above can be easily found. According

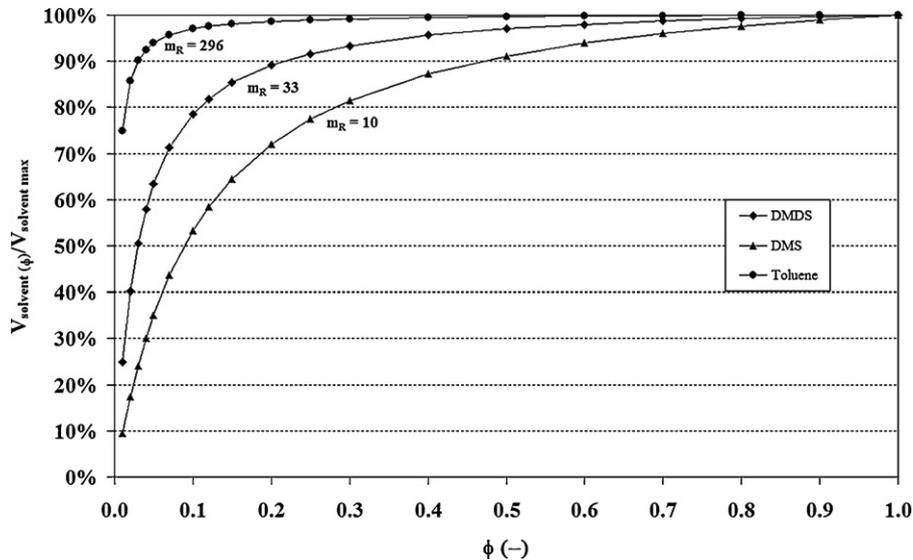


Fig. 4. Ratio of the silicone oil amount in the mixture to the maximum quantity needed for absorption in pure silicone oil versus silicone oil volume fraction.

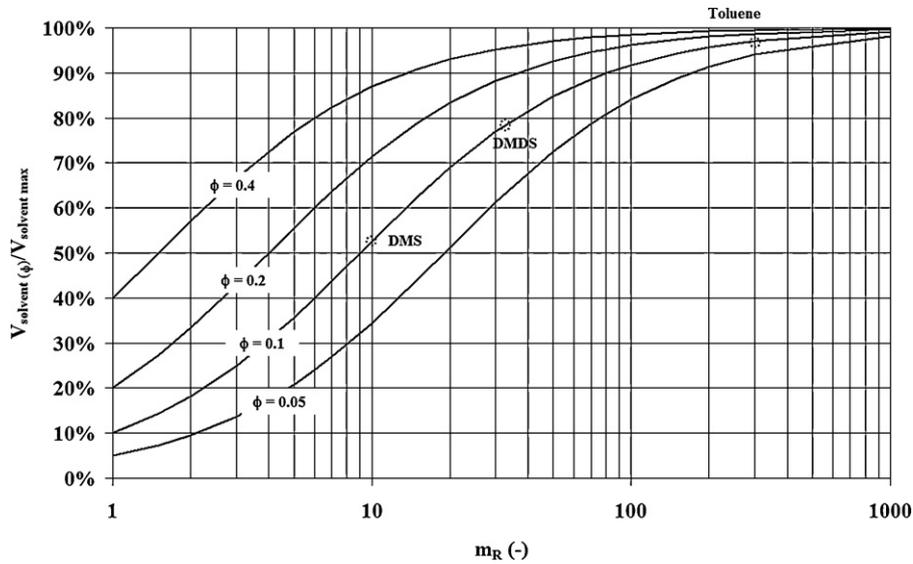


Fig. 5. Ratio of the silicone oil amount in the mixture to the maximum quantity needed for absorption in pure silicone oil versus VOC distribution coefficient.

to m_R values, Fig. 5 gives clear information about the advantages of using, or not, pure solvent for absorption. Generally speaking, for VOCs having a $m_R > 20$, the physical absorption must be carried out with pure silicone oil. However, although m_R is a good criterion for selecting the operating mode of absorption (water/silicone oil mixture or pure silicone oil), it is not enough to calculate the quantity of oil to use. As demonstrated in Appendix C, the amount of silicone oil needed for absorption is given by the following expression:

$$\frac{V_{\text{solvent}}(\phi)}{V_G} = A \frac{H_{\text{voc,water}}}{RT} \frac{\phi}{1 + \phi(m_R - 1)} \quad (14)$$

It can be seen that the amount (the flow rate) of silicone depends directly on: the gas flow rate, the absorption factor chosen and the partition coefficient of the VOC between air and water (i.e. the Henry's law constant). This quantity is also a function of m_R and ϕ . Fig. 6 presents an example of the evolution of (V_{solvent}/V_G) calculated for $H_{\text{voc,water}} = 200 \text{ Pa m}^3 \text{ mol}^{-1}$ (arbitrary value). This figure confirms that, for $m_R > 20$, the amount of silicone oil that must be used, whatever the silicone oil volume fraction, is equal to the maximum amount needed for an absorption in pure silicone oil. This

amount is given from Eq. (14) for $\phi = 1$:

$$\frac{V_{\text{solvent max}}}{V_G} = A \frac{H_{\text{voc,solvent}}}{RT} \quad (15)$$

In such a case, the amount of silicone oil does not depend on $H_{\text{voc,water}}$, but directly on $H_{\text{voc,solvent}}$. For the operating conditions corresponding to this study ($V_G = 10,000 \text{ m}^3 \text{ h}^{-1}$ and $A = 1.5$), the maximum amount of silicone oil is: $V_{\text{solvent max}} = 6.05 H_{\text{voc,solvent}}$ ($\text{m}^3 \text{ h}^{-1}$).

These results highlight that a VOC having both a large $H_{\text{voc,water}}/H_{\text{voc,solvent}}$ ratio (greater than 20) and a high affinity for silicone oil (partition coefficient $H_{\text{voc,solvent}}$ less than 3 or $4 \text{ Pa m}^3 \text{ mol}^{-1}$) can be satisfactorily trapped by pure silicone oil in an absorption column before being degraded by micro-organisms in a bioreactor. Such biological treatment could be effectively implemented in industries emitting large amounts of air loaded with a VOC (or a mixture of VOCs) satisfying the criteria above. However, if the mixture of VOCs does not satisfy these criteria (for instance, DMS is present), it will be necessary:

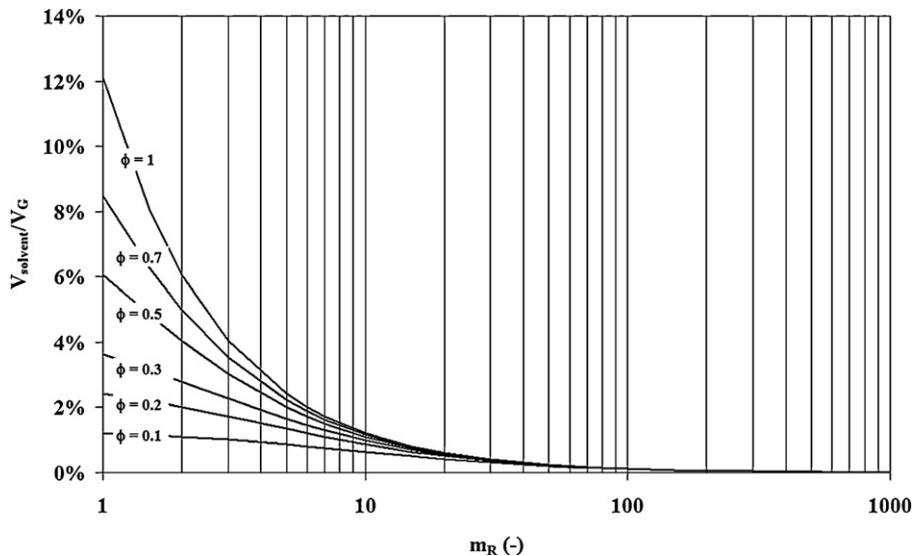


Fig. 6. Silicone oil amount needed for absorption (relative to the gas flow rate to be treated) versus VOC distribution coefficient for different silicone oil volume fractions ($H_{\text{voc,water}} = 200 \text{ Pa m}^3 \text{ mol}^{-1}$).

- (i) to design the process by taking into account the partition coefficients of VOCs with the lowest affinity for silicone oil. In this case, the contactor is necessarily too large for the absorption of the other considered VOCs,
- (ii) to choose a more suitable solvent for the mixture of VOCs to be treated, which may be difficult taking into account the properties that the solvent must display.

6. Conclusion

VOC absorption in water/silicone oil mixtures using a counter-current column has been considered; firstly, for DMDS, DMS and toluene and secondly, generalised to other VOCs.

For a given absorption factor, the amount of silicone oil needed for absorption has been calculated. For a VOC having a high affinity for silicone oil and a distribution coefficient $m_R > 20$ (the case of DMDS and toluene in this study), it is unwise to use a water/silicone oil mixture for absorption. It is preferable to use pure silicone oil in order to reduce operating costs. For a given temperature, the amount of silicone oil needed for absorption is proportional to the gas flow rate to be treated, to the absorption factor and to the VOC partition coefficient $H_{\text{voc,solvent}}$. The biological treatment of air loaded with these pollutants should be highly effective in an integrated system consisting of a countercurrent packed-bed absorption column combined with a two-phase partitioning bioreactor for pollutant degradation and solvent regeneration.

Appendix A. Calculation of the absorption factor versus ϕ

Combination of Eqs. (4)–(6) gives:

$$A = \frac{V_L RT}{G} \frac{1}{H_{\text{voc,mixture}}} \frac{\rho_G}{M_G} \quad (\text{A.1})$$

Assuming the ideal gas law:

$$G = \frac{PV_G}{RT} \quad (\text{A.2})$$

As:

$$P = RT \frac{\rho_G}{M_G} \quad (\text{A.3})$$

Introducing Eqs. (A.2) and (A.3) into Eq. (A.1) gives:

$$A = \frac{V_L}{V_G} \frac{RT}{H_{\text{voc,mixture}}} \quad (\text{A.4})$$

With:

$$\frac{1}{H_{\text{voc,mixture}}} = \frac{(1-\phi)}{H_{\text{voc,water}}} + \frac{\phi}{H_{\text{voc,solvent}}} \quad (\text{A.5})$$

Appendix B. Calculation of the generalised ratio

$V_{\text{solvent}}(\phi)/V_{\text{solvent max}}$

From Eq. (8), it follows:

$$A = \frac{V_L RT}{V_G} \left[\left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{1}{H_{\text{voc,water}}} \right] \quad (\text{B.1})$$

Multiplying the left and right members by ϕ gives:

$$\phi A = \frac{\phi V_L RT}{V_G} \left[\left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{1}{H_{\text{voc,water}}} \right] \quad (\text{B.2})$$

As $V_{\text{solvent}} = \phi V_L$:

$$\phi A = \frac{V_{\text{solvent}} RT}{V_G} \left[\left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{1}{H_{\text{voc,water}}} \right] \quad (\text{B.3})$$

For $\phi = 1$, $V_{\text{solvent}} = V_{\text{solvent max}}$. Eq. (B.3) becomes:

$$A = \frac{V_{\text{solvent max}} RT}{V_G H_{\text{voc,solvent}}} \quad (\text{B.4})$$

Eq. (B.3) divided by Eq. (B.4) gives:

$$\phi = \frac{V_{\text{solvent}}}{V_{\text{solvent max}}} \frac{[(1/H_{\text{voc,solvent}}) - (1/H_{\text{voc,water}})]\phi + (1/H_{\text{voc,water}})}{1/H_{\text{voc,solvent}}} \quad (\text{B.5})$$

$$\frac{V_{\text{solvent}}}{V_{\text{solvent max}}} = \frac{1/H_{\text{voc,solvent}}}{(1/H_{\text{voc,solvent}}) - (1/H_{\text{voc,water}}) + (\phi/H_{\text{voc,water}})} \quad (\text{B.6})$$

Multiplying the numerator and denominator of the right member by $H_{\text{voc,solvent}}$ gives:

$$\frac{V_{\text{solvent}}}{V_{\text{solvent max}}} = \frac{1}{1 - (H_{\text{voc,solvent}}/H_{\text{voc,water}}) + (\phi H_{\text{voc,solvent}}/H_{\text{voc,water}})} \quad (\text{B.7})$$

As $H_{\text{voc,solvent}}/H_{\text{voc,water}} = 1/m_R$, Eq. (B.7) becomes:

$$\frac{V_{\text{solvent}}}{V_{\text{solvent max}}} = \frac{1}{[1 + (1/m_R)((1/\phi) - 1)]} \quad (\text{B.8})$$

Appendix C. $V_{\text{solvent}}(\phi)$ calculation

The expression of the absorption factor is:

$$A = \frac{V_L RT}{V_G} \left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{V_L RT}{V_G} \frac{1}{H_{\text{voc,water}}} \quad (\text{C.1})$$

Multiplying the left and right members by ϕ gives:

$$\phi A = \frac{\phi V_L RT}{V_G} \left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{\phi V_L RT}{V_G} \frac{1}{H_{\text{voc,water}}} \quad (\text{C.2})$$

As $V_{\text{solvent}} = \phi V_L$:

$$\phi A = \frac{V_{\text{solvent}} RT}{V_G} \left(\frac{1}{H_{\text{voc,solvent}}} - \frac{1}{H_{\text{voc,water}}} \right) \phi + \frac{V_{\text{solvent}} RT}{V_G} \frac{1}{H_{\text{voc,water}}} \quad (\text{C.3})$$

$$\frac{\phi A}{RT} = \frac{V_{\text{solvent}}}{V_G} \left(\frac{1-\phi}{H_{\text{voc,water}}} + \frac{\phi}{H_{\text{voc,solvent}}} \right) \quad (\text{C.4})$$

$$\frac{V_{\text{solvent}}}{V_G} = \frac{\phi A}{RT} \frac{1}{((1-\phi)/H_{\text{voc,water}}) + (\phi/H_{\text{voc,solvent}})} \quad (\text{C.5})$$

Multiplying the numerator and denominator of the right member by $H_{\text{voc,water}}$ gives:

$$\frac{V_{\text{solvent}}}{V_G} = \frac{\phi A}{RT} \frac{H_{\text{voc,water}}}{H_{\text{voc,water}}(((1-\phi)/H_{\text{voc,water}}) + (\phi/H_{\text{voc,solvent}}))} \quad (\text{C.6})$$

$$\frac{V_{\text{solvent}}}{V_G} = \frac{\phi A}{RT} \frac{H_{\text{voc,water}}}{((1-\phi) + (\phi H_{\text{voc,water}}/H_{\text{voc,solvent}}))} \quad (\text{C.7})$$

As $m_R = H_{\text{voc,water}}/H_{\text{voc,solvent}}$:

$$\frac{V_{\text{solvent}}}{V_G} = A \frac{H_{\text{voc,water}}}{RT} \frac{\phi}{1 + \phi(m_R - 1)} \quad (\text{C.8})$$

For $\phi = 1$:

$$\frac{V_{\text{solvent}}}{V_G} = \frac{V_{\text{solvent max}}}{V_G} = A \frac{H_{\text{voc,solvent}}}{RT} \quad (\text{C.9})$$

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