Additional Determinations in a Potential Support Material for Toluene Biofiltration: Adsorption and Partition in the Nutrient Solution

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This paper studies the adsorption properties in wet and dry conditions of a potential support material for toluene biofiltration. The material was able to retain 2.5 times less toluene when the contaminated airflow was fed either water-saturated or devoid of moisture, which is an indication of the relative exposed surface area accessible for adsorption. The correlation coefficients between Freundlich-modelled and experimental values (R^2 = 0.98) suggest that, within the tested range of toluene concentrations, this model is valid to describe adsorption equilibrium and that n exponent is near 1 when natural material is used as adsorption bed. In addition, the air-liquid partitioning constant values of toluene in water and in a nutrient solution used for biomass acclimation were determined. The constant obtained for the nutrient solution ranged from 0.167 to 0.224 for liquid toluene mass concentration (γ_L) values ranging from 10.3 to 36.2 g m^{-3} at 298 K. By contrast, the constants in water varied from 0.221 to 0.277 for γ_L values ranging from 7.86 to 27.6 g m^{-3}.

Key words:
Toluene, adsorption, partitioning constant, biofilter support material

Introduction

The success of biofilters, also called vapour phase biological reactors (VPBR), relies on numerous biological, physicochemical and operational factors.

Chemicals to be treated by biofiltration should be biodegradable and relatively water soluble, as microorganisms responsible for the effective degradation of pollutants into harmless products live and grow in the aqueous biofilm around the packing material. More than 50 target gas components have been evaluated for biofiltration applications.[1] Inorganic compounds such as hydrogen sulphide and ammonia have been extensively studied in the literature and the removal efficiency reported is close to 100 % in many cases.[2–5] Volatile organic compounds (VOCs) such as toluene, ethylbenzene, xylenes, methanol, styrene, ketone and formaldehyde have also been successfully biodegraded.[6–10]

Regarding physicochemical factors, the most obvious function of the carrier or filter bed material is as a support structure for internal and/or external biofilm development.

Consequently, it should present several characteristics such as high surface area, high void fraction, high moisture retention capacity, low bulk density, balanced chemical composition, low cost and long life.[5,6,11] A high retention capacity of the pollutant by adsorption is also an additional and desirable property in the event of a possible system failure due to the drying of the bed material.

Most biofiltration research has been conducted on these fundamental aspects, but other additional tests are also helpful to understand the start-up and non-steady operation of bioreactors. *Zilli* et al.[12] concluded that the removal efficiency of toluene, close to 100 %, initially measured in the biofilters was due to the preliminary adsorption of the pollutant on the filter bed. Hence, the role of the carrier material to retain the pollutant by adsorption is relevant not only at a first step but also during operation. Many models describing biodegradation assume that microorganisms form a uniform biofilm on the exterior surface of the particles.[13] Quantities such as biofilm surface area or biofilm thickness are difficult to determine, although quantitative methods have been proposed in literature.[14] When moisture retention in the bed material is low, there are patches of biofilm that leave the exposed surface of the solid in direct contact with the air-stream. In this case, adsorption of the pollutant takes place on this exposed surface.

Evaluating the retention capacity of the carrier material will provide information about biodegradation and/or adsorption when low contaminant concentrations are fed into the system. The adsorption performance is expected to be very different for hydrophobic or hydrophilic compounds, whilst in wet conditions the liquid layer is very important in both

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cases, as the remaining exposed surface can be reduced dramatically. However, although a high adsorption capacity of the bed material is desirable as a safety measure for an operating biofilter, it can also be a disadvantage when inlet contaminant concentration suddenly decreases or stops, as reversible desorption will undoubtedly take place to a certain extent.

A further relevant study to be carried out refers to pollutant solubility in aqueous salt solutions or nutrient solutions. Biomass acclimation to the target contaminant is usually carried out in batch experiments, where microorganisms living in a nutrient salt solution are fed by pulses of the pollutant as the only carbon source. The results obtained by *Deshusses* and *Johnson*[15] suggested that biodegradation of VOCs in biofilters was influenced by pollutant availability (quantified by the Henry's law constant) and, to a lesser extent, by the hydrophobicity of the treated compound (octanol/water partition).

Hydrophobic alkylbenzenes such as toluene are moderately water soluble, but this relative solubility in the liquid phase depends on temperature, suspended solid concentration (SS), pH, salinity, oil content and the concentration of dissolved organic matter.[16] The salting-out effect of certain inorganic compounds on the solubility of toluene has been reported in literature, although the non-additive effect of salts on the solubility of toluene has also been found.[17]

Increasing the solubility of organic compounds in water is desirable for biofiltration purposes, but this may also pose a disadvantage, as contaminants such as toluene will be transferred to the biofilm at higher rates than O_2. Consequently, accumulation of the toxic pollutant in the biotic phase will occur and cellular damage will be caused by the prolonged exposure of the microbial community to the contaminant.[18] One alternative to this problem is the use of two-phase partitioning reactors.[19]

This paper focuses on measuring two additional parameters in a potential support material for treating toluene in biofilters. The determination of the adsorption capacity of the support material in wet and dry conditions will avoid overestimating biodegradation. The determination of the partitioning constant in the nutrient salt solution will control the amount of carbon source (toluene) accessible for the biomass in batch experiments.

Methods and materials

Adsorption study

The organic packing material used in this study as adsorption bed consisted of pig manure and sawdust, and its characterization can be found elsewhere.[20] This material has previously been used by the authors as support material in biofilters treating inorganic compounds.[5] It was sterilized in order to avoid biodegradation contributing to the adsorption/absorption study in wet conditions (T = 121 °C and t = 120 min).

The experimental runs were performed in triplicate in a laboratory-scale bioreactor, used as an adsorption column in this study (Fig. 1). Thus, the biofilter was a column of D = 0.05 m in diameter and L = 0.29 m in length and was made of PVC. Compressed laboratory air was humidified in a wa-

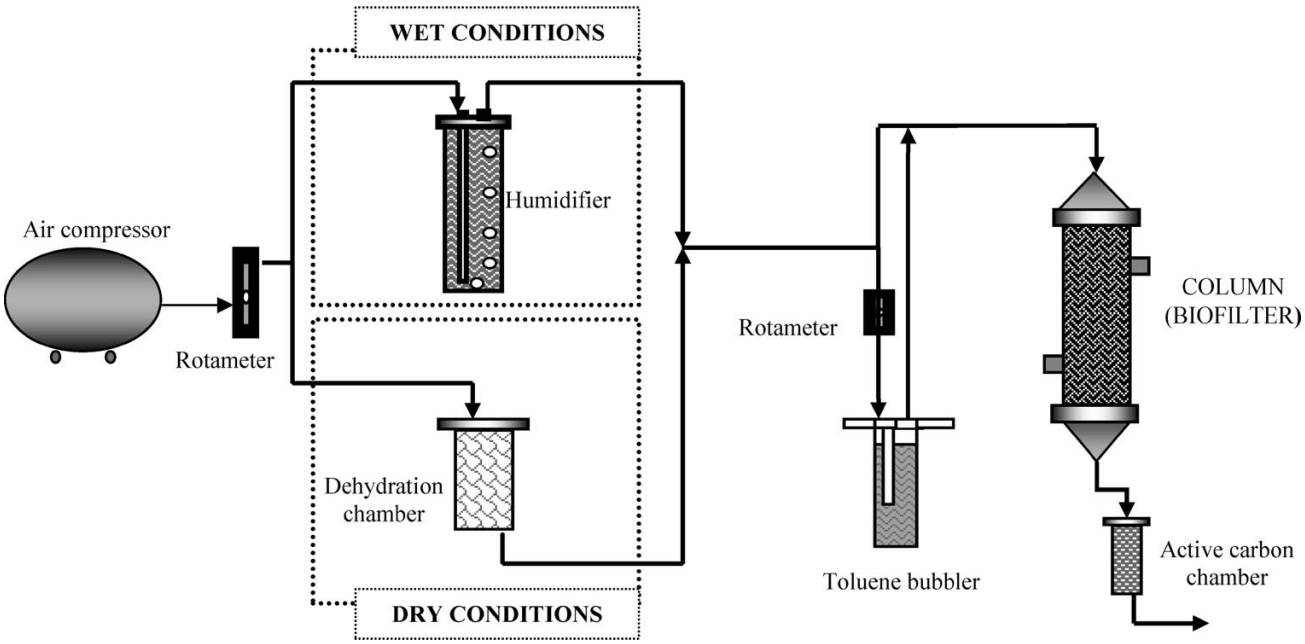


Fig. 1 – *Scheme of the experimental system for adsorption studies*

ter column to ensure that relative humidity exceeded 95 % for wet conditions. In the case of dry conditions, the compressed air was fully dried by being passed through a dehydration column filled with $CaCl_2$ and the support material was also dried at 105 °C for 24 h before use to ensure no water was present. The wet or dry airflow was then split into two fractions. The smaller portion of air was allowed to bubble through a liquid toluene container to generate the contaminated air stream. This stream was mixed with the larger portion of the airflow to generate a total gas flow ratio of $Q = 0.1$ m^3 h^{-1}, which was fed into the column or bioreactor (Fig. 1). Temperature was kept constant at 298 K.

After reaching saturation point in each case, clean air was fed into the columns in order to desorb the retained toluene. The inlet and outlet concentrations of the contaminant were measured during operation by taking air samples with a syringe (Hamilton, USA).

Toluene mass concentration was measured in a 6890N gas chromatograph (Agilent, Spain) equipped with a 30 m · 0.53 mm HP-PLOT 40 μm Q column and a flame-ionization detector (FID). Helium was used as the carrier gas. Injection port, oven and detection port temperatures were 200, 150 and 260 °C, respectively.

Determination of the partitioning constant

The partitioning constant was determined in water and in a salt nutrient solution by using the single equilibration technique (SET) developed by *Cheng* et al.[21] The salt macronutrient solution was prepared by adding 0.2 g KH_2PO_4, 0.8 g K_2HPO_2, 0.05 g $MgSO_4 \cdot 7H_2O$, 0.02 g $CaSO_4 \cdot 2H_2O$, 0.02 g $FeSO_4 \cdot 7H_2O$ and 1 g $(NH_4)_2SO_4$ to a litre of water. An amount of 5 cm^3 of another micronutrient solution (containing 2 g dm^{-3} $FeCl_2 \cdot 4H_2O$, 2 g dm^{-3} $CoCl_2 \cdot 6H_2O$, 0.5 g dm^{-3} $MnCl_2 \cdot 4H_2O$, 60 mg dm^{-3} $CuCl_2$, 50 mg dm^{-3} $ZnCl_2$, 50 mg dm^{-3} H_3BO_3, 2 g dm^{-3} HCO_3Na, 90 mg dm^{-3} $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 1 g dm^{-3} EDTA, 0.1 g dm^{-3} Na_2SeO_3, 0.1 g dm^{-3} $NiCl_2 \cdot 6H_2O$, 2 mg dm^{-3} HCl and 0.5 g dm^{-3} resarzurine $C_{12}H_6NNaO_4$) was added to one litre of the macronutrient solution in order to prepare the final salt nutrient solution. Table 1 lists certain parameters measured in the nutrient solution.

A volume of $V = 50$ cm^3 of water or nutrient solution was fed into a $V = 235$ cm^3 glass bottle provided with a Mininert valve. Before the tests, the inner volume of each glass bottle was determined by the water replacement method. Subsequently, a dose of 1, 2, 3 or 4 μl of toluene liquid (PANREAC, analytical grade) was injected into the bottle with a syringe (Hamilton, USA). A rotation speed of $s = 100$ min^{-1} in a magnetic stirrer was selected in order to mix the toluene completely with the water or nutrient solution. Although *Cheng* et al.[21] concluded that the redistribution of toluene into the gaseous and aqueous phase finished within a period of 12 h, a period of 24 h was selected in this experiment to ensure equilibrium between both phases. After equilibration, a sample of headspace was collected with a syringe. Temperature was kept constant at 298 K during experimentation.

Table 1 – *Parameters determined in the nutrient solution*

Parameters	Unit	Value
pH	–	6.8
conductivity at 25 °C, κ	mS cm^{-1}	2.85
density, ρ	kg dm^{-3}	0.989
turbidimetry	NTU	82
ionic strength	mol dm^{-3}	0.027
total solid concentration, γ_s	g m^{-3}	1830
total suspended solid concentration, $\gamma_{t,s}$	g m^{-3}	151

Toluene mass concentration was monitored by a 6890N gas chromatograph, as explained before.

Results and discussion

Adsorption

The adsorption/desorption curves were determined for different inlet mass concentrations of toluene (1.30, 2.39, 5.04, 6.48, 8.18, 10.17 and 11.07 g m^{-3}) when the contaminated airflow and packing material were dried (in the absence of moisture) (Fig. 2). In all cases, the breakthrough point was reached during the first hour of operation and total desorption also took place very quickly. On the basis of the results shown in Fig. 2, the amount of toluene adsorbed on the dry bed at equilibrium at 298 K was calculated, and the results ranged from

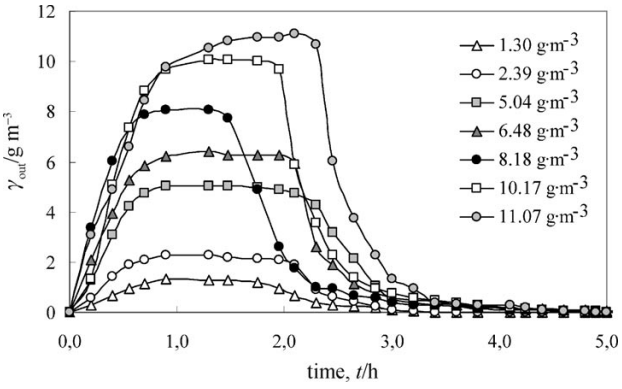
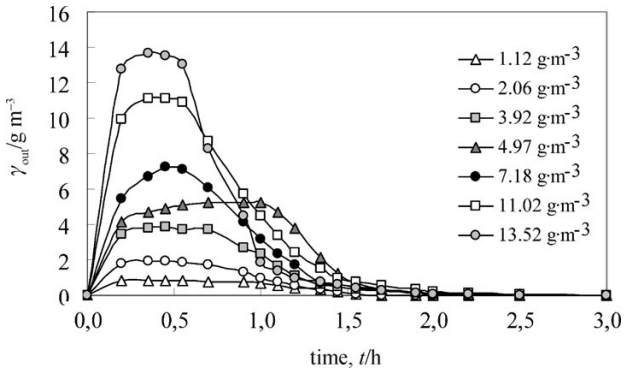


Fig. 2 – *Adsorption/desorption for toluene in dry conditions at 298 K*

168 to 1231 μg g^{-1} dry material. When comparing our previous results for H_2S using the same material in similar conditions, the retention of H_2S in the bed was 2250 μg g^{-1} dry material,[20] whilst the estimated value in this study for toluene is 60 μg g^{-1} dry material when a reference inlet mass concentration of 0.42 g m^{-3} is considered. This behaviour is explained largely by the different polarity of both molecules.

The second batch of experiments was carried out in wet conditions. Hence, the packing material had an initial moisture content of 28 % and the airflow fed into the column was close to water saturation. In this case, the combined action of adsorption on the remaining exposed surface of the material and the absorption on the liquid film were simultaneously evaluated at 298 K. The toluene inlet mass concentrations were 1.12, 2.06, 3.92, 4.97, 7.18, 11.02 and 13.52 g m^{-3} for a moist airflow rate of $Q = 0.1$ m^3 h^{-1}. The results of the outlet concentrations over time for contaminated and clear air feeding are shown in Fig. 3. The breakthrough point is reached more quickly than in the case shown in Fig. 2, which reveals that the retention capacity of the column in dry conditions is higher than in wet conditions. This is consistent with the quantification of the amount of contaminated air retained by the material, which ranged from 65.2 to 739 μg referred to one gram of dry material. In conclusion, the packing material is able to retain 2.5 times less toluene in wet as opposed to dry conditions, which is an indication of the exposed surface area accessible for adsorption. Accordingly, some authors[22] found that water mainly affects the adsorption of aromatic and aliphatic compounds by decreasing their retention.



F i g . 3 – *Adsorption/desorption for toluene in wet conditions at 298 K*

The data obtained in the two sets of runs were fitted to the Freundlich model. The equation used for this approach is as follows:

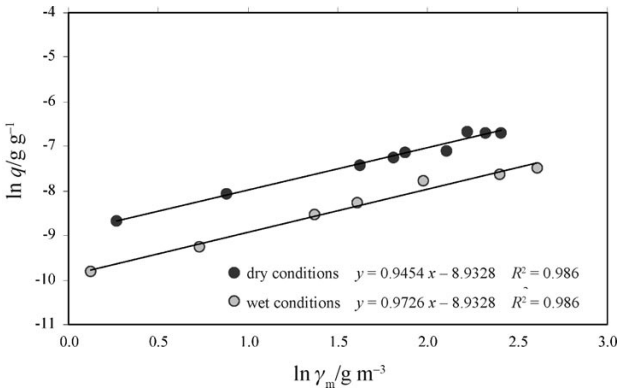
$$q = K_f \gamma_{in}^n \quad (1)$$

q is the amount of toluene retained on the material (g g^{-1}), γ_{in} is the inlet mass concentration of toluene (g m^{-3}) and K_f and n are the corresponding parameters of the Freundlich model. This equation can be rearranged in the linear form by taking the logarithm of both sides as:

$$\ln q = \ln K_f + n \ln \gamma_{in} \quad (2)$$

The calculations of the toluene retained in the material (q) were carried out according to the procedure used by *Delhomenie* et al.[23]

The theoretical isotherms and the correlation equations obtained according to eqs. (1) and (2) in wet and dry conditions are shown in Fig. 4. The correlation coefficients between Freundlich-modelled and experimental values ($R^2 = 0.986$) suggest that, within the tested range of toluene mass concentrations, this model is valid to describe both adsorption equilibria (at wet and dry conditions). A comparative study between the n Freundlich constant published in literature and those obtained in



F i g . 4 – *Adsorption isotherms (Freundlich) of toluene on the dry and wet support material*

T a b l e 2 – *Examples of n Freundlich constant for toluene adsorption.*

Adsorption medium	Freundlich constants
peat and perlite	n = 1.04 (moist bed)[24]
peat	n = 0.70 (moist bed)[25]
compost	n = 0.92 (moist bed)[23]
compost	n = 0.97 (moist bed)*
bituminous base activated carbon	n = 3.18 (dry bed)[26]
coconut base activated carbon	n = 3.68 (dry bed)[26]
compost	n = 0.95 (dry bed)*

* Present study

this study is shown in Tab 2. The *n* exponent is near 1 when natural material such as peat or compost is used, yet it is as high as 3.18 or 3.68 when activated carbon is used for toluene adsorption. Although the *n* value for dry and wet conditions is similar, the K_f constant is 134 (μg g^{-1}) · (m^3 g^{-1})$^{1/n}$ and 50.5 (μg g^{-1}) · (m^3 g^{-1})$^{1/n}$, respectively.

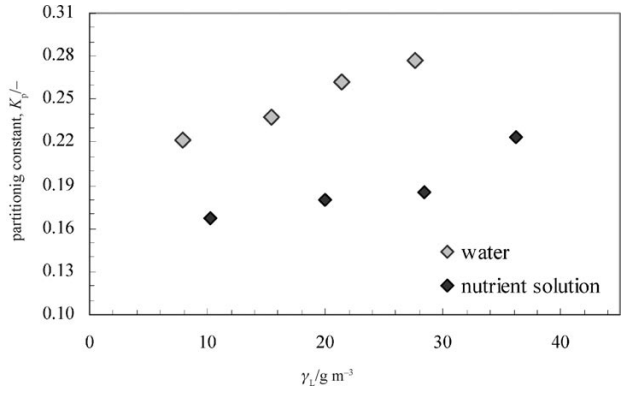
Partitioning constant

The toluene mass concentration at equilibrium at the interface between air and water is normally specified using a partitioning constant (K_p) as follows:

$$K_p = \gamma_G / \gamma_L \quad (3)$$

where γ_G is the gaseous toluene mass concentration in equilibrium with the aqueous phase at a constant temperature (298 K in this study) (g m^{-3}) and γ_L is the liquid toluene concentration (g m^{-3}). *Cheng* et al.[21] studied the effect on K_p of varying γ_L for several target aromatic VOCs and concluded that the difference between the solubility of hydrophobic and hydrophilic compounds in water determines the effect of concentration on K_p. However, Henry's law states that the K_p value of dilute solutions is constant; that is, K_p is independent of γ_L and in this case the solution can be classified as an "ideal solution".

The concentration effect on K_p was measured in water and in the nutrient solution that will subsequently be used for biomass growth. Fig. 5 shows the partitioning coefficient values at different liquid phase concentrations of toluene. The K_p value ranged from 0.221 to 0.277 for toluene concentrations in water ranging from 7.86 to 27.6 g m^{-3} at 298 K. These results are slightly higher than those reported by *Cheng* et al.,[21] whose K_p values ranged from 0.223 to 0.230 (almost constant) for γ_L values between 0.47 and 19.21 g m^{-3} at 300 K. *Görgényi* et al.[27] determined that the Henry's law constant ranged from 0.0740 to 0.8254 when temperature



F i g . 5 – *Variations of the partitioning constant (K_p) with γ_L for toluene at 298 K*

ranged from 275 to 333 K. *Lin* and *Chou*[28] proposed a value for the air-liquid partition constant of 0.271 at 298 K and also calculated the phase change enthalpy (17.51 kJ mol^{-1}) and the associated entropy change (52 J mol^{-1} K^{-1}). A similar single value of 0.268 at 298 K was found by *Dewulf* et al.[29] by using solid-phase microextraction techniques.

The coefficient values obtained for the nutrient solution (apparent partitioning constant) ranged from 0.167 to 0.224 for γ_L values ranging from 10.3 to 36.2 g m^{-3} at 298 K. As these partitioning constant values are lower than those in water, it is concluded that toluene solubility is higher in the nutrient solution than in water.

The experimental results obtained by *Peng* and *Wan*[30] showed that the dimensionless Henry's law constant for organic compounds such as toluene increased as concentration of inorganic salts such as NaCl in the solution increased. In fact, they found that the constant in water was 0.196 and 0.326 in sea water at 298 K and furthermore, the salting-out constant was determined. *Poulson* et al.[17] suggested that the non-additive effect of inorganic salts on the descreasing solubility of toluene was due to specific interactions between slightly polar toluene (dipole moment of 0.45 debyes) and ions in solution. In contrast, other authors[31,32] found that ammonia and ammonium ions significantly increased the solubility of certain compounds. *Görgényi* et al.[31] reported that ammonia solutions increased the solubility of 17 volatile organic compounds (including toluene) nearly linearly. This was explained on the basis that ammonia contributes to an easier cavity formation, ending up in increasing solubility with increasing solute volume. In fact, the poor solubility of hydrophobic compounds is explained in terms of energetic and cavity aspects. When a solute is dissolving, it has to displace molecules to make a cavity and to establish interactions between the solute and surrounding water molecules.[31] In this study, the most abundant salt in the nutrient solution is ammonium sulphate, and bearing in mind that the experimental pH of the solution is 6.8, the ammonia/ammonium equilibrium is displaced so that the predominant species is the cation. Thus, electrostatic interactions between ammonium and the slightly polar toluene may be responsible for the higher solubility of toluene in the nutrient solution.

Furthermore, it is well-established that dissolved organic matter, biomass and suspended solids (SS) in general, increase the solubility of hydrophobic organic contaminants in liquid solutions.[28,33] In this study, the nutrient solution has a content of inorganic suspended solids of 151 g m^{-3}, which is much lower than the SS values studied by other au-

thors.[28] Although no biomass is present in the nutrient solution (no dissolved organic carbon is present), suspended inorganic particles are responsible of the total turbidimetry measured in the nutrient solution (82 NTU). Hence, sorption of hydrophobic toluene on the suspended particles may also be responsible, to a certain extent, for the moderate decrease in the partitioning constant. The mass concentration of suspended solids is expected to be higher in the nutrient solution after adding the biomass to be grown, which means that biosorption will be greater and the partitioning coefficient of toluene is expected to be even lower than those obtained in this paper.

This conclusion is directly applicable in batch experiments for microorganism growth and in biofilters. The amount of toluene accessible for biomass to degrade in the nutrient solution of batch experiments is higher than that calculated by Henry's constant determined in water. Furthermore, bearing in mind that biofilters are fed with a constant inlet mass concentration of toluene in gas phase, the partitioning constant will determine the real concentration of toluene in the liquid phase or bioactive layer of the packing material accessible for biomass. Furthermore, oxygen mass transfer should be promoted carefully, as an accumulation of toluene in the biolayer with oxygen limitation will lead to irreversible microbial damage.

Conclusions

Besides the physicochemical characterization of the packing material and the control of operational parameters, other determinants are also helpful to understand the complex performance of biofilters.

Adsorptive properties (retention properties) of the filtering material will provide information about the behaviour of the material when the bed dries and reversible adsorption of the contaminant takes place on the exposed surface. In this study, an organic material rendered a toluene retention capacity ranging from 168 to 1231 μg g^{-1} material and from 65.2 to 739 μg g^{-1} in dry and wet conditions, respectively.

The air-liquid partitioning constant will provide information about the mass concentration of the contaminant in the liquid phase, being thus accessible for biomass to degrade. Hydrophobic compounds such as toluene are moderately soluble in water but, by contrast, toluene solubility is increased in the nutrient solution used to grow adapted biomass on batch experiments. The ratio between both partitioning constant (water/nutrient) is 1.36 at 298 K.

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List of symbols

D – diameter of biofilter, m
I_c – ionic strenght, mol dm^{-3}
K_f – Freundlich constant, mol dm^{-3}
K_p – partitioninig constant, –
L – lenght of biofilter, m
n – Freundlich index
q – absorption capacity, g g^{-1}
Q – volume flow rate, m^3 h^{-1}
s – rotation speed, min^{-1}
t – time, h
T – temperature, °C, K
V – volume, cm^3
γ – mass concentration, g m^{-3}
  γ_{in} – inlet mass concentration
  γ_{out} – outlet mass concentration
  γ_G – gaseous toluene mass concentration
  γ_L – liquid toluene mass concentration
  γ_S – total solid concentration
  $\gamma_{t,s}$ – total suspended solid concentration
κ – conductivity, mS cm^{-1}
ρ – density, kg m^{-3}

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