Online SIFT-MS measurement of a biofilter response to dimethylsulfide concentration step changes

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ABSTRACT. Volatile Organic Compounds (VOC) are responsible for photochemical smog and the depletion of the ozone layer. Biofilters are suitable to treat industrial emissions polluted with such VOC. This study analyzes online the performance of a biofilter treating an air stream contaminated with dimethylsulfide (DMS) and the response of the biofilter on DMS inlet concentration pulses and concentration step changes by using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS). These measurements were performed in a short period of time (40 hours) to keep the biomass constant.
After a start up period of 2 weeks, the biofilter was operated for 3 days in which several inlet loads (IL) and empty bed residence times (EBRT) were applied. The Michaelis-Mentens half saturation parameter, Km = 0.028 ± 0.002 g m^{-3}, and the maximal volumetric elimination rate, r_m = 7.23 ± 0.11 g m^{-3} h^{-1}, were calculated based on measurements at 35, 60 and 90 s EBRT.
The response of the biofilter to changes of the DMS inlet concentration by means of step and pulse variations was monitored.
The results illustrate that SIFT-MS is a suitable measuring technique to analyse online the performance of a biofilter. Due to the short analysis time it is possible to measure the biokinetic parameters, while keeping the biomass constant at different EBRT. As the bacterial growth had no influence on the determination of the biokinetic parameters during this experiment, it indicates that, the biokinetic parameters km and r_m are independent of the EBRT when the biomass remains constant.

INTRODUCTION

Dimethylsulfide (DMS) is a volatile organic compound (VOC) which is often found in waste gases of industrial sources and which is known to have a very low olfactory threshold that varies from 0.02 to 0.1 ppm between different persons. This laboratory study was set up to measure the immediate response of a biofilter on inlet concentration changes by means of step and pulse variations by using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS). Advantages of the SIFT-MS approach include the ability to measure VOCs online and the sensitivity to low ppb levels. At present, most studies on biofiltration utilize GC-MS technology[1], which usually needs a preconcentration step and typical analytical run times of at least 30 min to 1 hour. Due to this fast measuring method it is possible to monitor the immediate response of the biofilter on step and pulse variations of the DMS inlet concentration.

An important trend in biofiltration is to determine the Michaelis-Mentens half saturation parameter, Km, and maximal volumetric elimination rate, r_m, by using existing models[2-5], as these parameters may, differ considerably with those found in literature depending on the experimental conditions in which the parameters were obtained. As the bacterial cultures responsible for the degradation of DMS are known to be slow growers[6], it was possible to assume that bacterial growth was negligible during the short measuring period and had no influence on the determination of the biokinetic parameters.

MATERIALS AND METHODS

Set-up

An overview of the experimental set-up is presented in Fig. 1. A mixture of wooden dowels (l = 15 mm; d = 6 mm; 60 vol%) and compost (40 vol%) was used as carrier material in a cylindrical bioreactor composed of Plexiglas, with a total length of 580 mm and an internal diameter of 54 mm. The sludge used to inoculate the reactor came from a wastewater treatment plant (Ossemeersen, Ghent, Belgium) and was first preadapted with DMS. Afterwards the biofilter was also inoculated with a pure culture of *Hyphomicrobium VS*, known to degrade DMS and to be a slow grower with a doubling time of 24 hours[7].Air was loaded with DMS by using a syringe pump (New Era, infusion/withdraw NE 1000 Model) and it was pumped through the biofilter from bottom to top with flow rates ranging between 0.9 and 2.3 l min^{-1}.

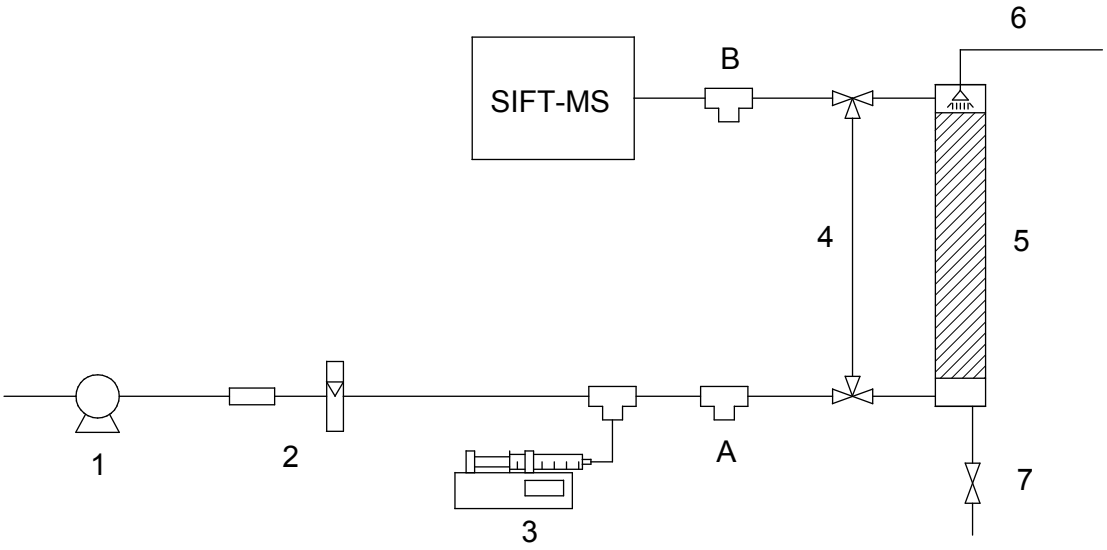


Fig. 1. Schematic diagram of biofilter. (1) Air pump, (2) mass flow controller and read-out unit, (3) syringe pump, (4) bypass, (5) biofilter, (6) humidifier, (7) leachate release, (A) sample port inlet, (B) sample port outlet.

Nutrients were added at the top of the reactor once a day. The necessary macro and micronutrients were incorporated using a pH buffered nutrient solution (pH 7) containing KNO_3, 10.7 g L^{-1}, KH_2PO_4, 3.0 g L^{-1}, K_2HPO_4, 3.0 g L^{-1}, $MgSO_4 \cdot 7H_2O$, 0.5 g L^{-1}, P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. Nutrients levels added were high enough to have a

C:N:P ratio of at least 100:5:1. (see reference 21 article macadamia). To humidify the reactor, 150 ml of water was added at the top of the reactor each day.

Process conditions
During a two week start-up period a constant air flow of 2.4 l min^{-1}, empty bed residence time (EBRT) = 33 s, and an inlet load (IL) of 5.1 g m^{-3} h^{-1}(inlet concentration 46.8 mg m^{-3}), were applied on the reactor. Once the outlet concentration remained stable for 3 days, several operational conditions were tested in the filter during a short period of only 3 days.

To determine the performance of the biofilter and the biokinetic parameters, DMS inlet concentrations were varied between 20 mg m^{-3} to 420 mg m^{-3} at gas empty bed residence times (EBRT) of 35, 60 and 90 s. The experimental sequence is summarized in Table 1.

Table 1. Operational parameters and sequence of the biofilter experiments

		IL (g m^{-3} h^{-1})							
		1.8	**2.3**	**4.5**	**6.4**	**6.7**	**11.0**	**12.8**	**15.5**
EBRT (s)	**90**	1	4	7	10	13	19	22	16
	60	2	5	8	11	14	20	23	17
	35	3	6	9	12	15	21	18	24

The main aim of the experimental design was to keep the IL constant and to measure the outlet concentrations at respectively 90, 60 and 35 s of EBRT till the outlet concentration reached a stable value. Once the outlet remained constant the biofilter was bypassed, so the corresponding inlet concentration could be determined by the SIFT-MS. Finally a new inlet condition was applied on the reactor. At the highest three IL the conditions were changed in a more randomized way, in order to confirm no measuring errors occurred by using the applied measuring pattern.

In order to monitor the immediate response of the biofilter on changes of the DMS inlet concentration by means of step variations, the EBRT was kept constant at 90 s and the IL was decreased stepwise from 16.7 to respectively 12.6, 11.3 and 4.11 g m^{-3} h^{-1}. The biofilter was first bypassed in order to measure the exact applied inlet concentration.

To determine the influence of a DMS inlet concentration pulse on the performance of the biofilter, 0.5 µl liquid DMS (0.42 mg) was injected at the inlet of the biofilter at three different EBRT, 35 s, 60 s and 90 s, while the biofilter was operated under a constant IL of 5.2 g m^{-3} h^{-1}. First the biofilter was bypassed and a pulse of 0.5 µl DMS was injected at sample port A, see Fig. 1. Then the outlet concentration of the biofilter was measured and a second pulse of 0.5 µl DMS was injected at the inlet of the filter, sample port A, to determine the response of the biofilter.

Analytical techniques

The DMS concentration in the gas flow at the inlet and outlet of the biofilter was monitored by connecting respectively the inlet and the outlet of the filter to the SIFT-MS. The standard SIFT-MS technique has been described in numerous publications[8-10], so a brief summary is given. In a Voice 200® (SYFT Technologies Ltd.) precursor ions H_3O^+, NO^+ and O_2^+ are generated in a discharge ion source, a specific mass is selected by a quadrupole mass filter and then injected as selected ionic species into fast-flowing He carrier gas in a flow tube. Determination of the counts per second (CPS) of the precursor ions and the resulting product ions, as a consequence of the reaction of the former with gas phase molecules, is performed by a downstream quadrupole mass spectrometer. To determine the DMS concentration the following product ions were measured: $(CH_3)_2S^+$ [NO^+], m/z = 62; $(CH_3)_2S^+$ [O_2^+], m/z = 62; $(CH_3)_2S.H^+$ [H_3O^+], m/z = 63; CH_2S^+ [O_2^+], m/z = 46; CH_3S^+ [O_2^+] m/z = 47. In order to prevent condensation of water vapour, the sample inlet lines are heated to ~ 373 K. He carrier gas pressure is 20 Pa at room temperature (296–300 K).

RESULTS AND DISCUSSION

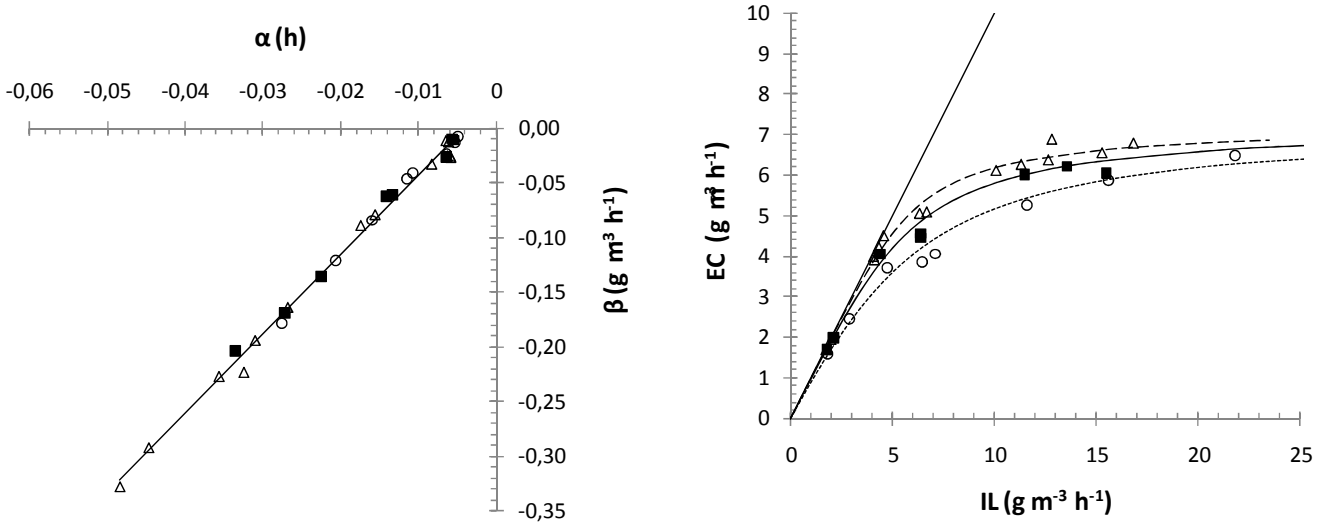
Biofilter performance

Using the Michaelis-Menten expression for the biological degradation reaction rate, see Eq.(1), Eq.(2) can be derived and the corresponding biodegradation kinetics Km, half saturation parameter, and r_m, maximal volumetric elimination rate, can be estimated from the obtained set of experimental data. This when assuming that steady-state conditions were reached for each applied inlet load and that the DMS removal rate followed the Michaelis-Menten kinetics[11].

$$r = -r_m \cdot \frac{C}{Km + C'} \tag{1}$$

$$C_{in} - C_{out} - Km \cdot \ln\left(\frac{C_{out}}{C_{in}}\right) - r_m \cdot \frac{V}{Q} = 0 \tag{2}$$

Plotting $\beta = \dfrac{C_{in} - C_{out}}{\ln\left(\dfrac{C_{out}}{C_{in}}\right)}$ versus $\alpha = \dfrac{EBRT}{\ln\left(\dfrac{C_{out}}{C_{in}}\right)}$, as shown in Fig. 2(a), resulted in a linear regression with r_m and Km the corresponding slope and intercept. A one-way analysis of variance (ANOVA)[12] show, that there is no significant difference between the intercepts and the slopes obtained at the different EBRT, at the 95 % significance level. For the slopes an F value of 0.44 was calculated which is much smaller than the tabled F value of 3.4. For the intercepts a F value of 1.7 was calculated, while the tabled value is 3.4. Linear regression of Eq.(2) using all the data resulted in a value for Km of 0.028 ± 0.002 g m^{-3} and a value for r_m of 7.23 ± 0.11 g m^{-3} h^{-1} independent of the EBRT.



(a) (b)

Fig. 2. (a) $\beta = \frac{C_{in} - C_{out}}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ vs. $\alpha = \frac{EBRT}{\ln\left(\frac{C_{out}}{C_{in}}\right)}$ and (b) EC vs. IL for an EBRT of (○) 35 s, (■) 60 s and (Δ) 90 s. Drawn lines are based on Eq.(3), (···) EBRT = 35 s; (—) EBRT = 60 s and (---) EBRT = 90 s.

The experimental values of the elimination capacity (EC) with respect to the IL at three values of EBRT are presented in Fig. 2(b). The drawn lines were calculated by Eq.(3), which was obtained from Eq. (1).

$$IL = \frac{EC}{1 - \exp\left[\frac{(EC - r_m)\cdot EBRT}{Km}\right]} \qquad (3)$$

By applying the obtained r_m and Km values in Eq. (3) the data at an EBRT of 35 s, 60 s and 90 s could be modelled. A maximal sample standard deviation of 0.24 g m^{-3} h^{-1} obtained between the experimental data and the data obtained by the model.

As the aforementioned biokinetic parameters are independent of the EBRT, it is possible to calculate the EBRT which has to be applied to reach a desired RE by Eq. (4).

$$EBRT = \frac{c_{in}\cdot\left(\frac{RE}{100}\right) - Km\cdot\ln\left(1 - \frac{RE}{100}\right)}{r_m} \qquad (4)$$

If a waste stream contains 0.5 g m^{-3} of DMS, an EBRT of 2.23 min will be needed to reach a RE of at least 50 % and 4.3 min to reach a RE of at least 90 %, see Fig. 3. This is a useful tool for industrial applications, because it is possible to calculate the flow or the volume of the reactor which is needed to reach a sufficient degradation. As these measurements were done at a constant biomass, it is clear that the RE can still increase, once the bacteria growth becomes higher and more adapted.

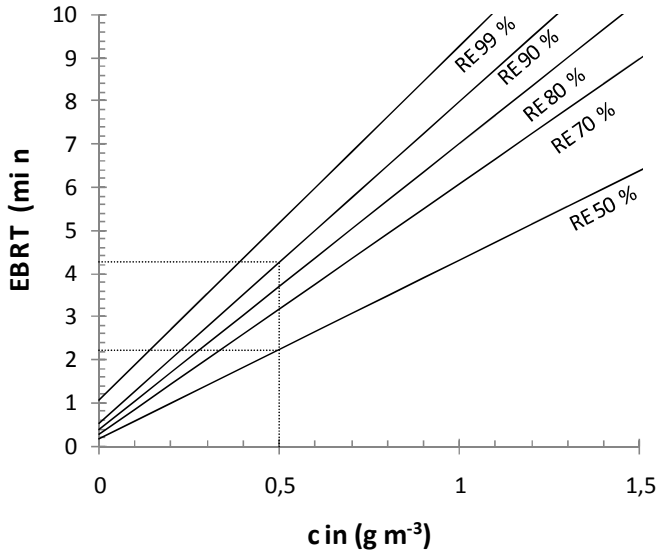
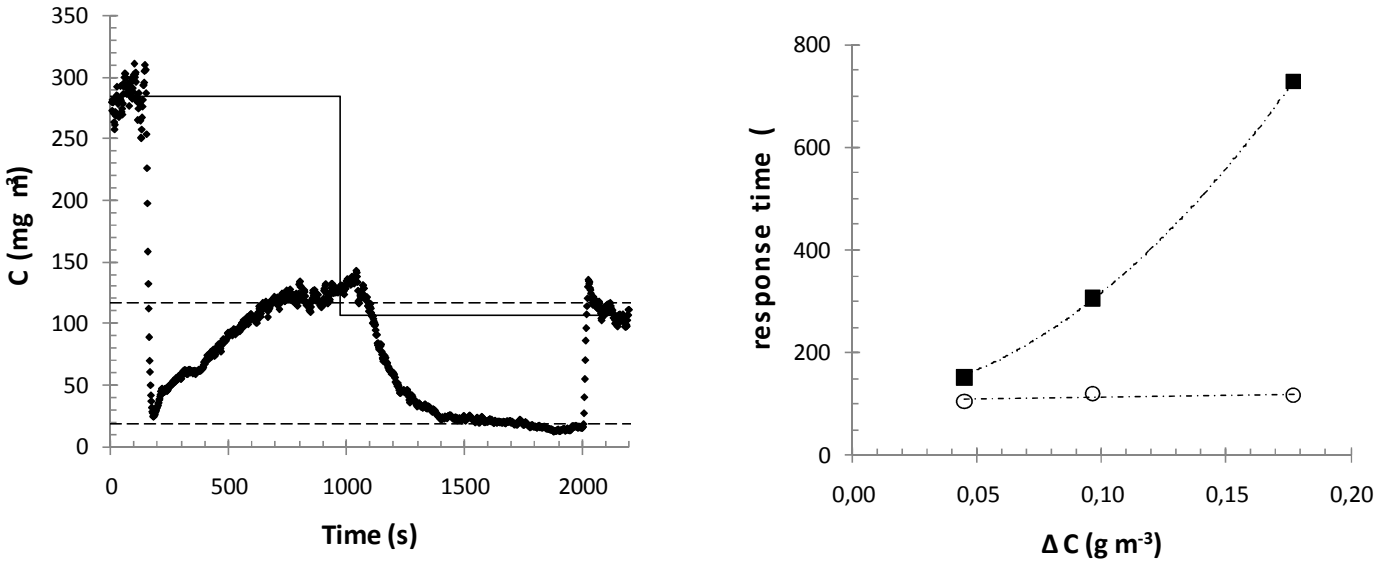


Fig. 3. EBRT vs. inlet concentration for different RE.

Step response experiment

SIFT-MS is used to investigate the response of the biofilter on an applied concentration step, see Fig.4(a).



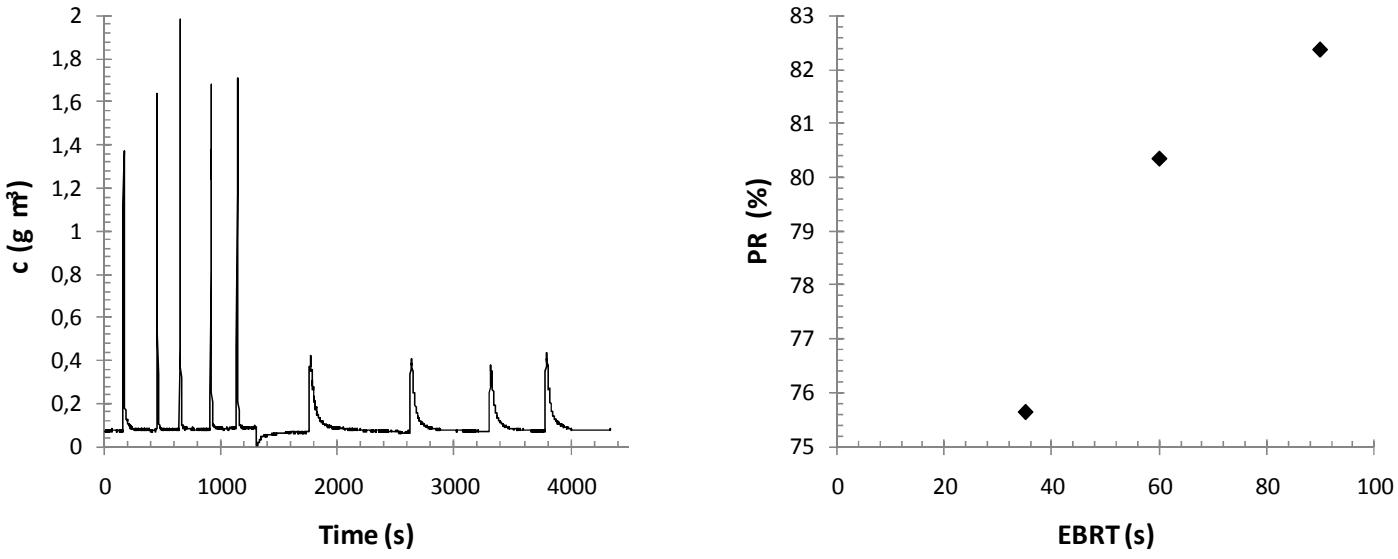
(a) (b)

Fig. 4. (a) Step experiment at 90 s EBRT with (—) the applied concentration step at inlet, (---) RT_5 and RT_{95} and (◆) measured points with SIFT-MS. (b) Response vs. applied concentration step for (○) RT_5 and (■) RT_{95}. Dashed lines are shown to guide the eye.

From 0 to 150 s the biofilter was bypassed, to check if the inlet concentration was stable, 284 ± 14 mg m^{-3}. At 150 s, the SIFT-MS measured the DMS biofilter outlet concentration. Once the outlet signal was stable, 122 ± 6 mg m^{-3}, the inlet concentration was lowered to 107 ± 6 mg m^{-3} at 973 s. At this inlet concentration, the outlet concentration lowered to 14 ± 1 mg m^{-3}. The following response times (RT) could be calculated: RT_5 = 117 s and RT_{95} = 727 s. With RT_5 and RT_{95} respectively the time where 5 % and 95 % of the total concentration change between the two stable outlet concentrations was reached lowered with the time where the new inlet concentration was applied. RT_5 indicates how fast the biofilter will respond on a concentration change, while RT_{95} indicates how fast the biofilter will reach a stable concentration again. Independent of the applied concentration step at fixed EBRT, the time to react on a concentration step, will be constant, constant RT_5, while it takes longer for the biofilter to reach a stable value with an increasing concentration step, higher RT_{95}, see Fig. 4(b).

Pulse response experiment

When injecting a pulse of 0.5 µl DMS at the inlet of the biofilter a sharp defined peak was visible at the inlet stream of the reactor with a high pulse concentration, e.g., 1.68 ± 0.22 g m^{-3} for pulses at an EBRT of 35 s, see Fig. 5(a). Once the peak passed through the column, it became much lower and broader due interaction with the packing material, but the total area underneath the outlet peak stayed the same as the one underneath the inlet peak. This means that the biofilter was not able to degrade any additional DMS caused by the pulse injection, but the maximum concentration at the outlet of the biofilter reduced significantly, only 0.41 ± 0.03 g m^{-3} at an EBRT of 35 s. The higher the EBRT, the higher the peak reduction (PR), lower maximum concentration at the outlet, and the broader the outlet peak, see Fig. 5(b).



(a) (b)

Fig. 4. (a) Pulse experiment with DMS pulses at inlet and outlet of the biofilter for 35 s EBRT and (b) PR vs. applied EBRT

CONCLUSIONS

Using the SIFT-MS as online measuring equipment it was possible to determine the biokinetic parameters of the lab-scale biofilter in only 3 days, while in standard approaches this can take weeks[11]. Due to the slow growth rate of the *Hyphomicrobium VS* it was possible to assume that the biomass, which is responsible for degrading the DMS remained constant during these measurements. The biokinetic parameters, with Km = 0.028 ± 0.002 g m^{-3}, the half saturation parameter and r_m = 7.23 ± 0.11 g m^{-3} h^{-1} the maximal volumetric elimination rate, are independent of the EBRT. These biokinetic parameters can be used to determine the reactor volume in order to obtain a sufficient removal, when the total volumetric flow rate and concentration are known.

Applying a DMS concentration step at the inlet of the reactor, the outlet of the biofilter will change very fast, but the higher the applied concentration step, the more time the biofilter needs to reach a stable value again. When injecting a pulse of DMS at the inlet of the biofilter, the reactor will not be able to degrade the additional DMS, but due to the interaction with the packing material, the maximal concentration of the pulse will lower significantly. The higher the EBRT, the higher the peak reduction and the lower the maximal outlet concentration.

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