Increasing the performance of biotechniques by upstream treatment with non-biological techniques

Smet Erik[a41], Jacobs Pieter[a], Marescaux Gregory[b] and Deboosere Stefaan[a]

[a]Trevi nv, Dulle-Grietlaan 17-1, B-9050 Gentbrugge (Belgium)

[b]Trevi sarl, C.I.T. – 53, Avenue de l'Europe, 59223 Roncq (France)

ABSTRACT

The performance and the application field for biotechniques as e.g. biofilters can be strongly increased by combining them with non-biological waste gas treatment systems in an intelligent way. In this article, it is illustrated that the injection of ozone gas upstream the bioreactor can strongly increase the performance of biotechniques for volatiles as e.g. styrene, limonene, &-pinene, isobutene and isoprene, and this due to a partial chemical oxidation of these volatiles. Also scrubbers and activated carbon filters can optimise the removal of pollutants when installed upstream biotechniques due to the selective removal of toxic compounds and/or balancing strong fluctuations in contaminant concentrations.

KEYWORDS

biofiltration; ozone; peakshaving; oxidation; scrubber

---

[41] Corresponding Author: ESmet@trevi-env.com

INTRODUCTION

Biotechniques in general and biofilters in particular are widely used in the industrial world, and this mainly for the abatement of odorous and VOC-containing waste gases. Biofiltration consists of a mass transfer process of the pollutant from the gas phase towards the wet biofilm, followed by a microbiological oxidation process of the pollutant in a biofilm that is mobilized on an organic carrier material. Actually, there are three prerequisites for a biotechnique to be successful in a specific situation: the pollutant should be biodegradable, the pollutant should at least be slightly water soluble and the pollutant concentration should not be too high or too fluctuating in concentration profile.

With regard to the biodegradability, some volatile compounds can only be degraded under anaerobic conditions (e.g. perchloroethylene) or using cometabolic microbiological processes (e.g. trichloroethylene). Next to that, competitive inhibition can occur in biofilters loaded with complex waste gases [Smet et al., 1997], yielding for instance a sequential degradation of first aldehydes, then organic sulphur compounds and finally terpenes upon biofiltration of mixed waste gases.

With regard to the water solubility, it is often stated that biotechniques can only be used for pollutants having a dimensionless Henry constant below a value of 1 à 10. This would mean that e.g. biofiltration of some alkenes is very difficult or impossible.

Finally, it is important to note that high contaminant concentrations or strong fluctuations in contaminant concentrations in a waste gas often adversely influence the effectiveness of bioreactors for waste gas treatment.

In the following, results of lab-scale, pilot-scale and full-scale experiments are given, showing that the performance and the application field for biotechniques can be strongly increased when non-biological waste gas treatment systems as ozone injection, activated carbon filtration or scrubbers are installed before the biotechniques in an intelligent way. The reason for this is that these non-biological techniques can change the waste gas composition in such a way that it becomes much more susceptible for biological degradation in the biotechnique.

PARTIAL OXIDATION OF VOLATILES BY OZONE INJECTION IN THE GAS PHASE

Kinetics of oxidation

Ozone is a gas with strong oxidative power that is often produced on-site due to its relative instability. Ozone has a high dimensionless Henry constant of 3.5 at 20°C, while its odour threshold value is 20 à 40 ppmv.

For industrial applications, electrical discharge ozone generators are used most often, applying oxygen gas or air as a source of oxygen. Producing ozone from

oxygen gas requires about 10 kg O_2/kg O_3 and ± 10 kWh/kg O_3. Producing ozone from air requires ± 20 kWh/kg O_3.
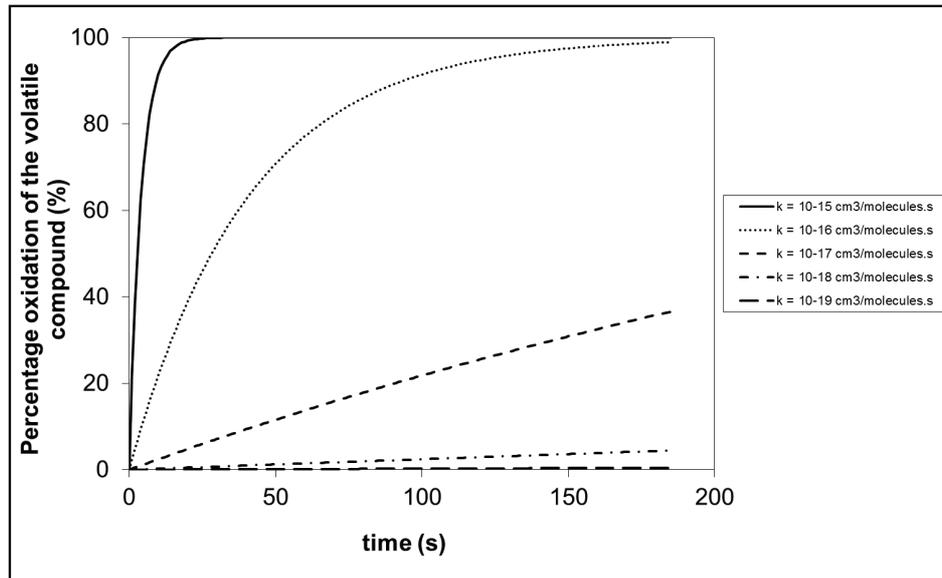
Figure 4: Theoretical oxidation rate of volatiles as a function of contact time and k-value (cm³/molecules.s) at an ozone concentration of 10 ppmv
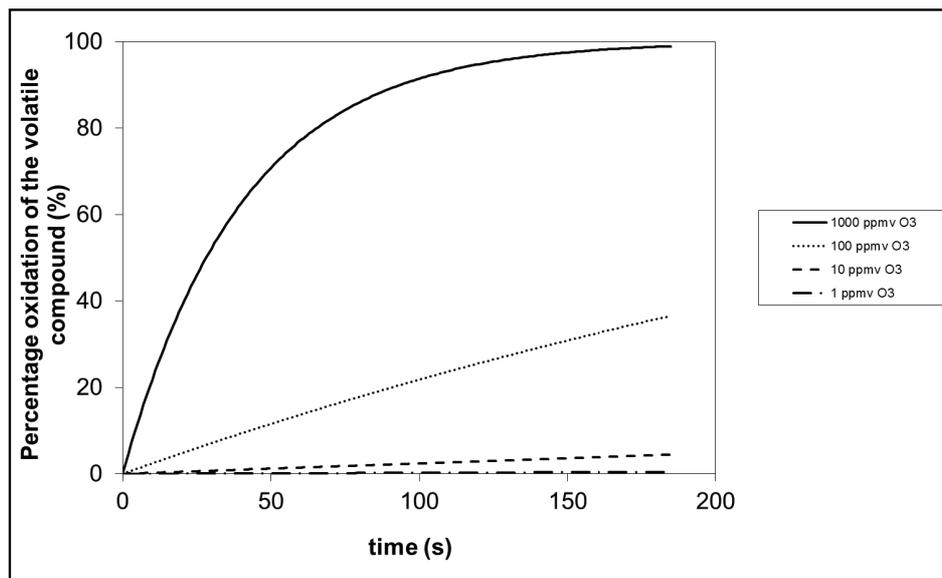
Figure 5: Theoretical oxidation rate of a volatile with k-value 10^{-18} cm³/molecules.s as a function of the ozone concentration applied.

The kinetics of the oxidation of volatile compounds with ozone is most often described as a second order reaction. Second order reaction rate constants for the reaction of ozone with several volatiles are reported in the atmospheric chemistry literature [Atkinson and Carter, 1984]. Application of ozonisation for waste gas treatment is only relevant for compounds with a k-value of about 10^{-17} cm³/molecules.s or higher, unless very high ozone concentrations and/or gas contact times can be realised. Indeed, ozone concentrations up to 1000 ppmv (2000 mg/m³)

are required in order to obtain oxidation of a volatile with a k-value of about 10^{-18} cm^3/molecules.s within several seconds (see Figure 4 and Figure 5).

Some compounds with a relative high k-value are mentioned in Table 8. Among the compounds with a k-value above 10^{-18} cm^3/molecules.s, there are alkenes, terpenes, amines, acrylates, hydrogen sulphide, styrene,… Based on our experience, the removal efficiency for several of these compounds in biotechniques is rather low. As a result of this, a pretreatment with ozone could make these volatiles susceptible for a biological treatment since the partial oxidation products will be more biodegradable and/or water soluble in comparison with the original products.

TABLE 8: REACTION RATE CONSTANTS FOR SOME VOLATILES (ATKINSON & CARTER, 1984)

Compound	*k-value (cm^3/molecule.s)*
Isobutene	$1.5 \ 10^{-17}$
isoprene	$1.5 \ 10^{-17}$
α-pinene	$6.0 \ 10^{-17}$
limonene	$6.4 \ 10^{-16}$
styrene	$2.5 \ 10^{-17}$
trimethylamine	$1.0 \ 10^{-17}$

Ozonisation of styrene

Lab-tests were done with 2 plexiglass columns, loaded with humidified and styrene containing air. The second column was filled with wood root material as a biofilter carrier material. The superficial gas residence time in the biofilter was ± 30 s. Ozone was dosed at the bottom of the first plexiglass column. This first column was the reaction chamber for the ozone oxidation, yielding a contact time of ± 42 s.

In a first experiment, the influent styrene concentration was installed at 940 mg/m^3, giving a styrene load to the biofilter reactor of ± 112 g/m^3.h. Without ozone addition, a removal efficiency of ± 50% was obtained over the biofilter (Figure 7). Upon gradually increasing the ozone dosing, the styrene concentration at the outlet of the biofilter gradually decreased.
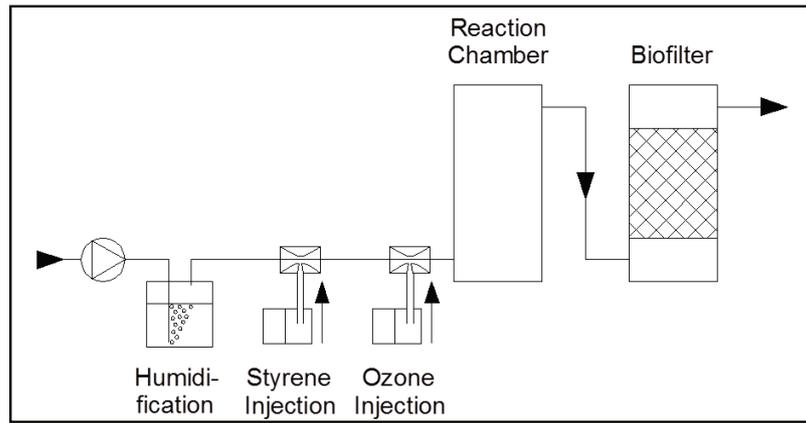
Figure 6: Set-up of the lab-scale experiment
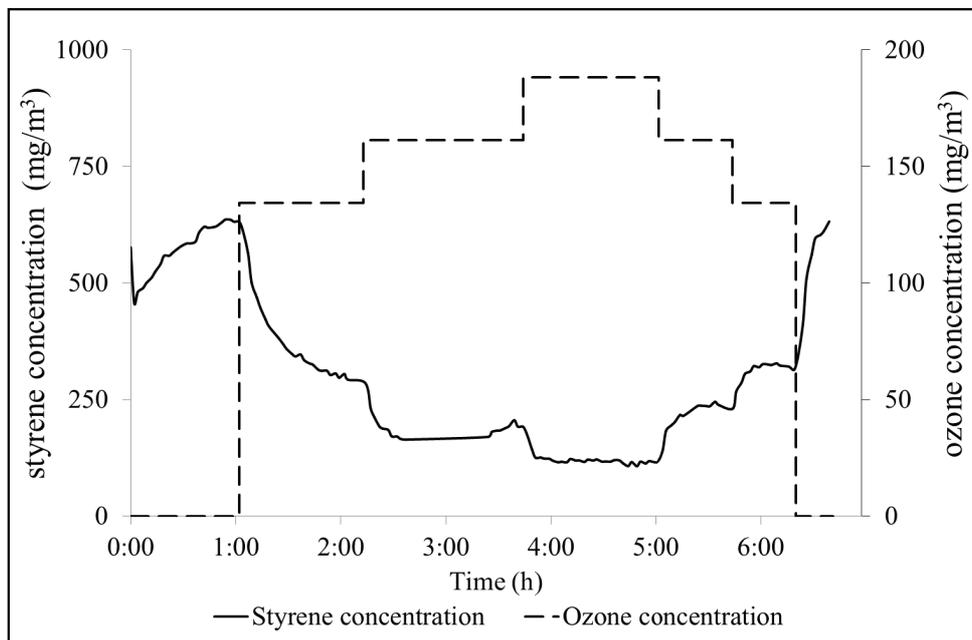
Figure 7: Effluent styrene concentration (mg/m^3) after the biofilter as a function of the amount of ozone injected (mg/m^3) before the biofilter.

Important observation was the 'benzaldehyde' odour at the outlet of the ozone reaction chamber, while this odour was not observed at the outlet of the biofilter. Benzaldehyde and formaldehyde are the expected partial oxidation products for styrene ozonisation (see Figure 8). The Henry constant for both benzaldehyde ($H_{25°C}$ = 0.0011) and formaldehyde ($H_{25°C}$ = 0.000014) is much lower than for styrene ($H_{25°C}$ = 0.11). This can be an explanation for the strongly increased styrene removal efficiency in the biofilter upon injection of ozone before the bioreactor. Next to that, biofilters in general have high removal efficiencies for aldehydes, such as benzaldehyde.

No rest ozone was observed at the outlet of the biofilter during the test, illustrating that the organic material in the biofilter not only degrades the partial oxidation products of styrene ozonisation but also eliminates the remaining ozone concentrations in the waste gas.

Figure 8: Partial oxidation of styrene by ozone.

In a second experiment, about 75% removal efficiency was obtained in the biofilter at an organic loading rate of 97 g/m^3.h (818 mg/m^3 styrene) without ozone addition (Figure 9). Upon addition of 322 mg/m^3 of ozone, a 100% removal efficiency for styrene was obtained. Upon stopping the ozone addition, the removal efficiency of the biofilter immediately returned to its original value. During the high ozone addition conditions, $\pm$ 10 mg/m^3 O$_3$ was detected at the outlet of the biofilter, illustrating only a minor ozone breakthrough at these very high input concentrations. Nevertheless, no inhibition of the microbiological oxidation was observed. Even upon adding ozone during several hours, no inhibiting effects of the high ozone dosing on the biofilter were observed (data not shown).
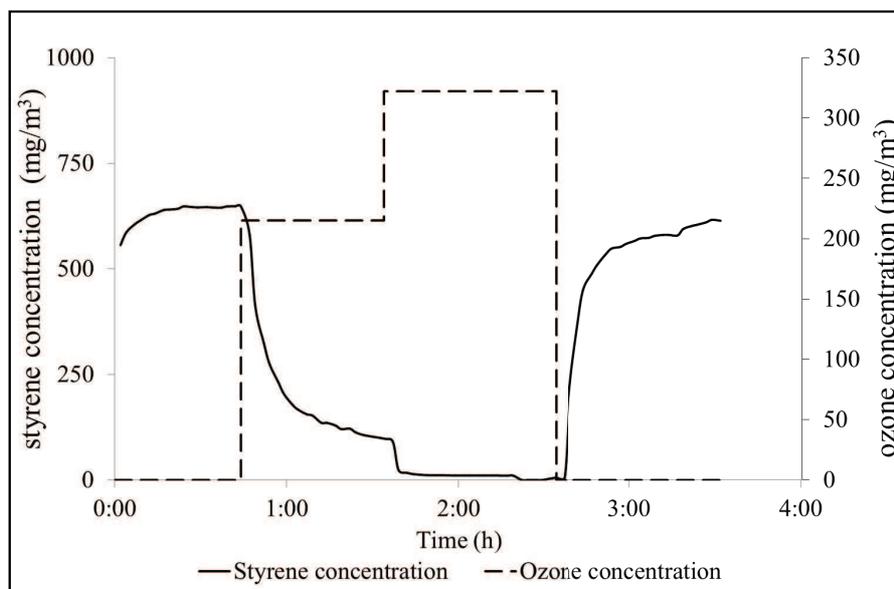
Figure 9: Effluent styrene concentration (mg/m^3) after the biofilter as a function of the amount of ozone injected (mg/m^3) before the biofilter.

Ozonisation of terpenes

A full-scale air humidifier + biofilter was loaded with a mixture of odorous volatiles. The surface loading rate to the biofilter was high (> 200 m^3/m^2.h), yielding a low superficial gas residence time of $\pm$ 25 s. Based on the GCMS-measurements, it was observed that the biofilter was heavily loaded with odorous compounds (> 5 g VOC/m^3.h). While the removal efficiency for most other groups of volatiles was acceptable, there was no removal efficiency observed for the terpenes (most important compounds: α-pinene and limonene). This is most probably due to the outselection on the biofilter carrier material of the terpene degrading micro-

organisms by the micro-organisms that degrade the 'easily' biodegradable compounds in the waste gas.

Pilot tests were done on-site with a small-scale ozone generator (capacity 60 g/h O_3). Ozone was injected upstream of the biofilter reactor, yielding a contact time of ± 20 s between the injection point and the biofilter. It was observed that the elimination capacity in the biofilter for the terpenes increased from 0% to 41% upon addition of a stoichiometric amount of ozone (stoichiometric in comparison with the terpene load). Apparently, the amount of ozone required is much higher than the theoretically calculated amount that is based on a 1:1 stoechiometric reaction. The most probable explanation for this is that ozone also reacted with other volatiles in the waste gas and/or with organic material/biomass that was present on the synthetic carrier material in the air humidifier. Based on this observation, a full-scale ozone generator with capacity 300 g/h O_3 was installed. Several weeks after installation and operation, GCMS-results were performed over the biofilter at 30% and 50% capacity of the new ozone generator. In both conditions, near 100% terpene removal efficiency was observed, while very high (98%) olfactometric odour removal efficiencies were observed. Surprisingly, also ± 100% terpene removal was observed after switching off the ozone generator during 30'. According to us, this illustrates that ozone not only reacts with some volatiles in the waste gas also stimulates the microbiological activity on the biofilter material itself when it is dosed during several days or weeks. This was also observed by others [Wang et al., 2009].

Ozonisation of alkenes

In a humid waste gas stream containing both chlorinated compounds, alkanes and alkenes, the effect of ozone addition on the removal of alkenes in a biotrickling filter was investigated. The main alkenes were isobutene (k 1.5 10^{-17} cm^3/molecules.s) and isoprene (k 1.5 10^{-17} cm^3/molecules.s). Without ozone injection, almost no removal of alkenes was observed in the biotrickling filter.

Ozone was injected upstream of the bioreactor, yielding a reaction zone of ± 20 s. As can be seen in Figure 10, more than 95% removal of alkenes can be obtained in the ozone reaction zone when there is a rest ozone concentration of about 10 ppmv (= ± 20 mg/m^3) at the entrance of the biotrickling filter. The amount of alkene removal was 2.5 à 3.5 kg/h upon the injection of ± 2.5 kg/h of ozone. As expected due to their very low k-values, no oxidation of the alkanes or chlorinated compounds was observed in the ozone reaction zone.

At the entrance of the biotrickling filter, 2-methyl-2-propenal and aceton were detected as the main volatile ozonisation degradation products in the gas phase. Contrary to the alkenes, however, these volatile partial oxidation products were eliminated in the biotrickling filter.

Due to the cooling of the humid waste gas in the ozone reaction zone, a lot of condensate was produced. This condensate was strongly concentrated with COD during the ozone addition test. The total COD-load in the condensate was estimated

to be ± 2.6 kg/h. The main pollutant in the condensate water was acetic acid, being a partial oxidation product of the alkene oxidation.
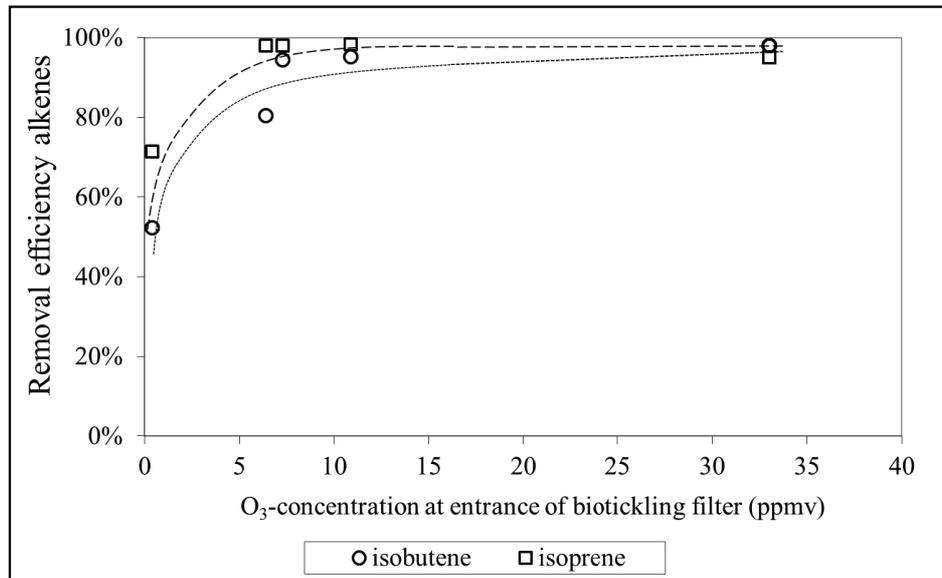
Figure 10: Alkene removal efficiency as a function of the rest concentration ozone at the entrance of the biotrickling filter.

PEAK SHAVING OF FLUCTUATING POLLUTANT CONCENTRATIONS USING ACTIVATED CARBON

Strong fluctuations in contaminant concentrations often adversely influence the effectiveness of biotechniques. A well-known example is the emission profile of solvents in paint spray booths. Dimensioning of a bioreactor based on these peak concentrations would yield very oversized and expensive installations. In this case, the use of a peakshaver in front of the biotechnique can have a pronounced positive effect. A peakshaver consists of a reactor filled with a selective adsorbent. During the peak emission of the volatile, the adsorbent will temporarily adsorb the pollutant, while a desorption will occur from the peakshaver towards the biotechnique afterwards.

This was illustrated in a full-scale biotechnique realization at a spray booth plant. A biofilter was realized for the removal of toluene from these waste gases. Before the biofilter, an activated carbon filter was realized, giving a superficial gas contact time of ± 2.5 s. The activated carbon filter was placed before the air humidifier of the biofilter. This is important since moisture will strongly reduce the adsorption capacity of the carbon filter. Figure 11 illustrates the strong impact of the carbon filter on the emission profile: the biological filter is loaded with a constant pollutant concentration due to the presence of the peak shaver. Provided a good dust filter is realized before the carbon filter, no replacement of the carbon is required since the contaminant will be desorbed once the peak concentration has gone. An important additional advantage of this peakshaver is that a gradual VOC-desorption will also take place during periods without production activity (weekends, holidays,…),

meaning that the biofilter will remain active during these 'inactivity' periods and will degrade part of the volatiles that were captured during the working period.
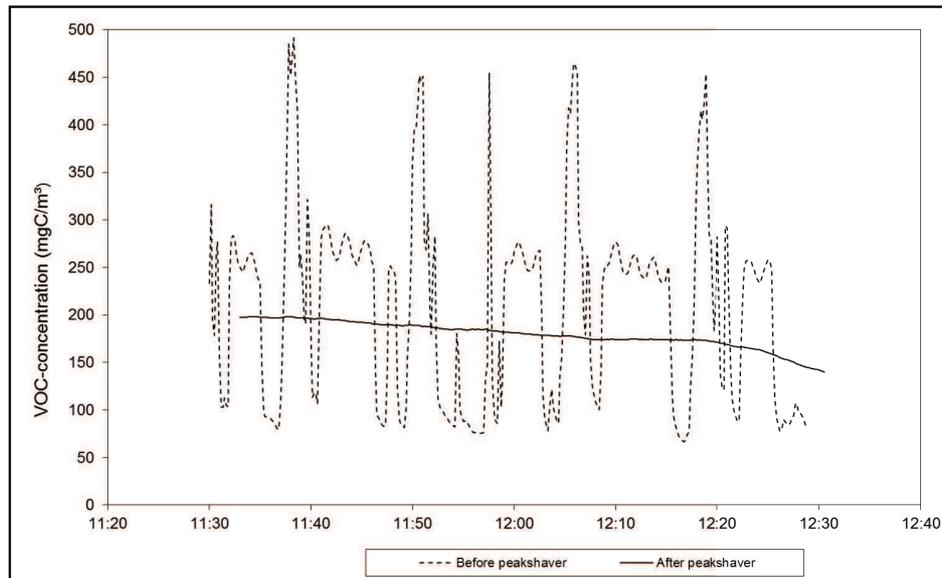
Figure 11. Effect of an activated carbon peak shaver on the VOC-emission profile (pollutant: toluene).

SELECTIVE REMOVAL OF A HIGHLY CONCENTRATED POLLUTANT

Several odorous waste gases contain one specific compound in a high or very high concentration (10 to 1000 mg/m^3), while the remaining odorants are present in very low (1-1000 $\mu g/m^3$) concentrations. Well-known is for instance the occurrence of high ammonia (NH_3) concentrations in composting waste gases, high hydrogen sulfide (H_2S) concentrations in the non-condensable waste gases of a rendering plant and high hydrogen chloride (HCl) concentrations in the waste gases originating from hydrolysis processes. Although H_2S and NH_3 can easily be degraded in a bio(trickling) filter, their presence in high concentrations can have a strong impact on the dimensioning of the bioreactor. The presence of HCl in an odorous waste gas will, on the other hand, result in a strong acidification and desactivation of the bioreactor.

In some cases, it is worth to evaluate the combination of two biotechniques in order to remove mixed waste gases. This is for instance the case for waste gases loaded with both H_2S and volatile organic compounds. Two bioreactors are required in order to separate the acidophilic H_2S-oxidising micro-organisms and the acidophobic VOC-degraders. In Figure 12, it is shown that a biotrickling filter, using lava stones as a carrier, can obtain high H_2S-removal efficiencies in the ventilation waste gas stream from a digestion plant under fluctuating input concentrations (0-250 ppmv).
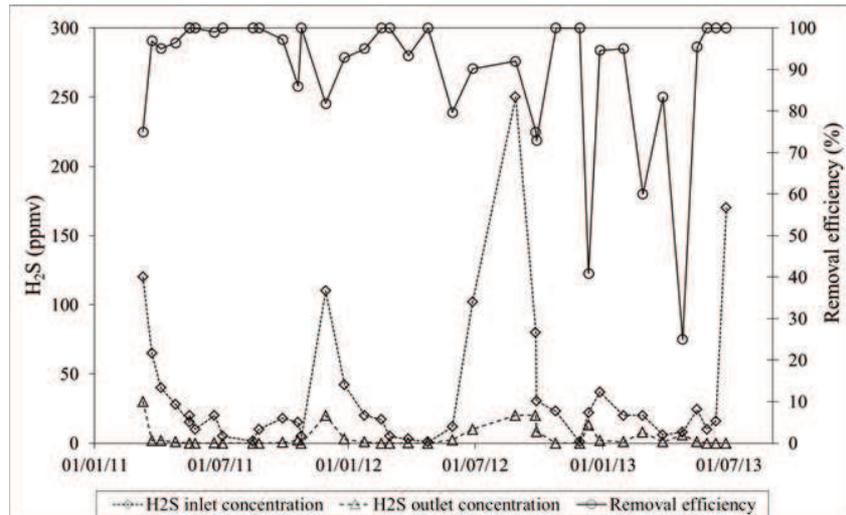
Figure 12: Inlet and outlet H₂S concentration (ppmv), together with the H₂S removal efficiency (%) of a lava trickling filter, loaded with ventilation waste gas from a digestion plant

Moreover, the sulphuric acid production in the lava filter due the microbiological H_2S-oxidation (sulphuric acid) resulted in a 'chemical' co-scrubbing of NH_3 from the waste gas. The superficial gas residence time in the lava filter was 60 seconds, while the irrigation flow was 15 l/m^2.d. In the biofilter that was positioned after this lava trickling filter, an optimal removal of organic volatiles was observed and no acidification of the biofilter carrier material was observed.

Most often, however, it is required to remove the highly concentrated pollutant in a chemical scrubber, while the remaining pollutants can be degraded in the subsequent bioreactor. In this case, an acid scrubber is used to remove ammonia, while a caustic scrubber is required for H_2S- or HCl-removal. For the removal of high concentrations of volatile organic sulphur compounds, a caustic oxidative scrubber is most often applied.

REFERENCES

[Atkinson and Carter]   Atkinson, R., Carter, W., 1984, "Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions", *Chemical Reviews*, 84, 437-470.

[Smet et al., 1997] Smet, E., Van Langenhove, H., Verstraete, W., 1997, "Isobutyraldehyde as a competitor of the dimethyl sulfide degrading activity in biofilters", *Biodegradation*, 8, 53-59.

[Wang et al., 2009] Wang, C., Xi, J., Hu, H., Yao, Y., 2009, "Stimulative effects of ozone on a biofilter treating gaseous chlorobenzene", *Environ. Sci. Technol.*, 43, 9407-9412.