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Novel waste gas treatment system able to cope with poorly water soluble VOC, fluctuating loads and biomass accumulation

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ABSTRACT. The objective of this project is to solve major challenges in the biological waste gas treatment by developing a novel process. These challenges are:

- load fluctuations of volatile organic compounds (VOC)
- treatment of poorly water soluble VOC and
- excessive biomass accumulation

The waste-gas treatment is split in two process steps: (i) the removal of the VOC from the gas phase and (ii) the microbial degradation. The VOC and oxygen are removed from the waste gas by a membrane-based absorption. This operation buffers load fluctuations and enables a constant feed of VOC and oxygen to the bacteria.
In the second process step the VOC are degraded in a membrane based biofilm reactor. A bacterial biofilm grows on the membrane and degrades the VOC and the oxygen buffered in the absorbent. A nutrient solution overflows the biofilm, introducing shear stresses on the biofilm surface and thereby removing excessive biomass to prevent the reactor from clogging.
The bacteria are supplied with oxygen and VOC through the membrane to the base of the biofilm. This creates a biofilm with the most active zone on the membrane. This activity profile allows discharging inactive biomass form the reactor.

1 INTRODUCTION

The emissions of volatile organic compounds (VOC) are becoming an increasing regulatory concern. In the year 2001, the large amount of 70'000t/a of anthropogenic VOC were emitted to the environment only in Switzerland (SAFEL 2003). Most VOC, which are emitted are likely to be harmful to human health, and they contribute to substantial damage on fauna and flora (Delhomenie and Heitz, 2005). Another indirect problem, caused by some VOC, is the formation of ozone in the troposphere by solar irradiation during summer time.
A certain fraction of these emissions cannot be eliminated, simply because they stem from private households or open systems. In the mentioned study 20% of the emissions stemmed from private households, 80% from the industry. If the emissions of the industry are analyzed based on the source, it becomes evident that the printing and paint

industry causes a big fraction (approximately 30%). These industries often use badly water soluble solvents, and the waste gas streams are often subject to load fluctuations.

1.1 Challenges of current waste gas treatment techniques

Biofiltration is an attractive technique for the purification of VOC contaminated waste gas. In spite of the big variety of waste gas treatment systems as well as of the extensive research carried out in this field, it is generally accepted that biological waste gas treatment systems show major challenges, which are not yet solved. A process is needed that is able to cope with the following challenges:

- VOC load fluctuations in the waste gas stream
- hydrophobic VOC and
- excessive biomass accumulation

Biological waste gas treatment systems are sensitive to transient feed conditions and process shut-downs (Al Rayes *et al*., 2001; Cox and Deshusses, 2002). Periods of low concentrations or process shutdowns can harmfully affect the biology in such a way that the reactor needs a long time (several days to a week) to fully recover its normal activity (Martin and Loehr, 1996). High peak concentrations can be toxic to the bacteria in the reactor and exceed its treatment capacity. In both cases, waste gas leaves the reactor untreated and contaminates thereby the environment (Weber and Hartmans, 1995).

This effect is even pronounced treating poorly water soluble compounds. These VOC feature high air-water partition coefficients, which cause low water concentrations and hamper the removal from waste gas (Brindle and Stephenson, 1996).

Clogging of fixed film bioreactors caused by excessive biomass growth is one of the main obstacles to the industrial application of biological waste gas treatment (Sorial *et al*., 1995; Weber and Hartmans, 1996; Cox and Deshusses, 1999). Due to rapid biomass accumulation in the reactors the pressure drop increases, leading finally to the shutdown of the system. At the same time, pollutant removal declines, mostly because of the decrease in interfacial area for mass transfer (Alonso *et al*., 1997).

1.2 Concept of the novel system

The VOC are removed from the contaminated waste gas by a membrane based absorption. The VOC, together with oxygen from the waste gas, diffuse through the membrane, separating the gas from the absorbent, and are readily buffered in the absorbent. This buffering is introduced to remove the VOC from the waste gas independently of load fluctuations and of microbial performance at that time. The total volume of the absorbent is virtually ideally mixed. The VOC and the oxygen are therefore transported by convection in the absorbent. In the second process step the VOC are degraded in a membrane based biofilm reactor. This second membrane separates the absorbent from the mineral medium. An aerobic biofilm grows on the mineral medium side of this membrane and degrades the VOC buffered in the absorbent. The mineral medium overflows the biofilm; on one hand delivering the nutrients and trace elements, necessary for bacterial growth, on the other hand introducing shear stresses on the biofilm surface, thereby removing excessive biomass to prevent the reactor from clogging.

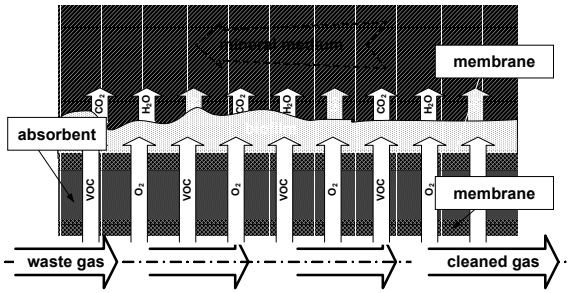

Figure 1. The concept of the novel waste-gas treatment.

The VOC reach the biofilm by diffusing through the membrane. The necessary oxygen for the aerobic, microbial degradation stems from the absorbent as well, since oxygen is buffered along with the VOC. This feed of the VOC and oxygen to the base of the biofilm creates an 'inverse' biofilm. The base layer, close to the membrane, is the most active zone. This activity profile over the biofilm thickness is different from natural biofilms, where the most active layer is usually the top part, close to the nutrient medium. This inverse activity profile is advantageous. The flow of the medium introduces shear stresses on the biofilm surface and removes thereby the top layer of the biofilm, containing mostly inactive biomass, by erosion or sloughing. The active base layer is not harmed during this process and therefore the microbial activity is kept high at all times.

2 MATERIALS AND METHODS

2.1 Experimental facility

The set-up is built using flat membranes for the absorption as well as for the bioreactor unit. The advantages of using membranes in the presented reactor are, besides the formation of an 'inverse' biofilm, (see section 1.2):

- an exact phase separation (there is no danger of cross-contamination between the two separated fluids, *e.g.* dust particles in the gas, absorbent droplet entrainment, or emulsion of absorbent and biomass suspension)
- the flow profile along a flat surface in a channel is known (this allows to estimate the influence of shear stresses on the biofilm erosion).
- the use of flat membranes does not impose any restrictions on the choice of the membrane material (often distinct geometrical forms are only available in a certain membrane material).

The described process is realized in an experimental facility by locally separating the absorption and the biological degradation step (see Figure 2). This is mainly done to be able to plan and to optimize both unit operations separately and due to the fact that there are no 'double membranes' available meeting the needs of the concept. The waste-gas stream and the absorbent are brought in contact in the absorption-module. A membrane separates the gas from the absorbent phase. The target VOC and oxygen are withdrawn from the waste-gas, across the membrane, and buffered in the absorbent. The absorbent is carried in a closed, well mixed loop. This loop connects the absorption-module with the bio-module. The desorption of the buffered substances takes place in the bio-module.

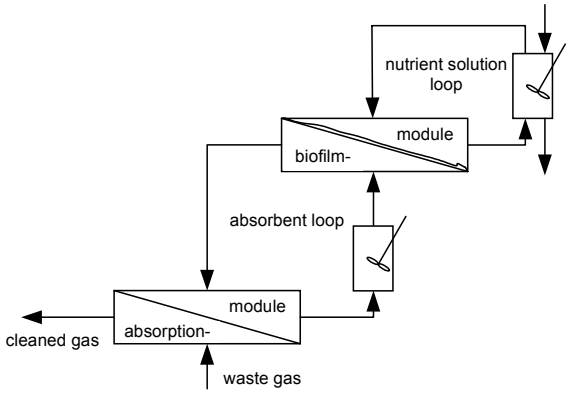

Figure 2. The simplified flow sheet of the experimental set-up.

Bacteria grow immobilized in a biofilm, directly on the membrane, separating the aqueous from the absorbent phase, where they degrade the buffered VOC. The aerobic bacteria receive the necessary oxygen, along with the VOC, only from the absorbent, across the membrane. The lacking nutrients (N, P, trace elements) stem from the nutrient medium overflowing the biofilm. The concept plans to introduce shear stresses on the biofilm surface to prevent the reactor from clogging. The shear stresses are introduced by creating a constant stream of the nutrient medium along the membrane or rather the biofilm. The aqueous phase is carried in a loop. A certain fraction of the culture medium has to be constantly replaced. A feed stream carries fresh medium to the reactor, while a bleed stream discharges, at the same rate, culture medium.

2.2 Materials and dimensions

Toluene is chosen as the model VOC. The artificial waste gas is produced using a loading unit, featuring a gas flow controller and a mass flow controller as well as an evaporator (Bonkhorst, Ruurlo, The Netherlands).

A novel, ultrathin, dense poly dimethyl siloxane (PDMS) membrane (CM-CELFA, Schwyz, Switzerland) is applied. The dense PDMS membrane is reinforced by means of a wire grating incorporated into the membrane structure for mechanical stability. The membrane features a total thickness of only 50 µm. The grating is made of chromium steel wires with diameters of 18 µm. The distance between the square grids is 30 µm and the wire grid is calendered to a final thickness of only 30 µm. The membrane areas amount to 0.18 m^2 and to 0.27 m^2 for the absorption- and for the bio-module, respectively.

The selected absorbent is silicone oil (AK50, Wacker-Chemie GmbH, München, Germany). The silicone oil features small gas-absorbent partition coefficients (c^g/c^a) for toluene (0.001 at 30°C) and for oxygen (5 at 25°C). The total volume of absorbent amounts to 7 L. The nutrient solution, overflowing the biofilm, is chosen to be the minimal medium M9 (Sambrook and Russell, 2001) without an additional carbon source. M9 contains the following concentrations of salts dissolved in deionized water: 32 g/l $Na_2HPO_4 \cdot 7H_2O$, 7.5 g/l KH_2PO_4, 1.25 g/l NaCl, 2.5 g/l NH_4Cl. Furthermore, 1 ml/l US* trace element solution (Panke *et al*., 1999) is added.

The reactor is inoculated with two well characterized bacterial strains, known for their ability to degrade toluene. The strains are *Pseudomonas putida* F1 (ATCC 700007, DSMZ 6899) and *Rhodococcus globerulus* PWD1 (NCBI 13325).

2.3 Measuring methods

The toluene gas concentration at the reactor inlet is taken on from the loading unit. The toluene concentration in the gas at the outlet of the reactor is measured using a flame ionization detector (FID) (VE7, J.U.M. Engineering, Karlsfeld, Germany). Based on the assumption that toluene is the only organic carbon source in the gas, this analysis can be used to calculate the toluene gas concentration at the outlet of the equipment. The zero-point is calibrated with nitrogen (5.0); the sensitivity calibration is done using a calibration gas made of propane (8066 ppm) in nitrogen (5.0) (PanGas, Dagmersellen, Switzerland).

The toluene concentration in the silicone oil is measured off-line by means of high performance liquid chromatography (HPLC) (Alliance 2690, Waters AG, Rupperswil, Switzerland) equipped with a photodiode array detector (PDA) (996, Waters). A packed phenyl-column (Nova-Pak® Phenyl 4µm 3.9x150 mm Cartridge, Waters) with acetic acid ethyl ester as the mobile phase is employed to perform the analyses. The samples are run in an isocratic mode. The total flow rate is 1 ml/min. The detection wavelength is set to 260.5 nm. The analyses are carried out at ambient temperature. The silicone oil samples are taken using a glass syringe equipped with a PTFE plunger (Hamilton, Bonaduz, Switzerland) directly from the absorbent loop. The samples are stored prior the analysis in 2 ml-HPLC glass vials sealed with PTFE lined silicone rubber septa (Infochroma AG, Grosshoechstetten, Switzerland).

The toluene concentration in the nutrient medium is measured off-line by means of gas chromatography (GC) (Varian 2000, Waters AG, Rupperswil, Switzerland) equipped with an FID Detector. A capillary column (Zebron ZB-628, 6 % cyano propyl phenyl, 94 % dimethyl polysiloxane, 30 m, 0.53 mm inner diameter, 3 µm film thickness, Brechbuehler, Schlieren, Switzerland) with helium (5.0) as the carrier gas (PanGas, Dagmersellen, Switzerland) is used. The analysis is done using ethanol as internal standard. The injector temperature is set to 120°C, the column pressure to 0.7 bar. The temperature cycle run in the oven is as follows: 40°C for 2.5 min, then the temperature is increased to 70°C at 10°C/min. A further increase in temperature to 140°C at 20°C/min is carried out before ending with a holding period of 2 min. The retention time for ethanol and toluene is 1.9 and 7.3 min, respectively. The aqueous samples are taken directly from the nutrient medium loop of the reactor (the sampling and the storage procedure is analogous to the one in the silicone oil (see this section above).

The biofilm thickness is measured by means of a laser distance sensor (LDS1-010, Raytec Systems AG, Chur, Switzerland). The laser operates at a wavelength of 780 nm, the focus point of the laser on the target surface features a diameter of approximately 50 µm and the accuracy of the available laser distance sensor is 25 µm. The principle of using laser distance sensors for investigating the thickness of a biofilm is summarized by *e.g.* Vinage and von Rohr (2003). In the course of the presented study the described principle is applied to measure the biofilm thickness *in situ.* The measurements are done through the cover glass of the channel as well as through the aqueous phase. The laser distance sensor is mounted on two linear-track guides (LF5, Heeb Electro AG, Küsnacht, Switzerland and 426 with SM-25, Newport GmbH, Darmstadt, Germany). These linear-track guides are installed on top of each other, and displaced against each other by an angle of 90°. This allows obtaining data points displaced by 0.5 mm from each other of a biofilm area of 23x280 mm^2.

3 RESULTS AND DISCUSSION

3.1 Reactor performance

The reactor is successfully run for a period of 150 days. A biofilm, degrading toluene develops on the membrane in the bio-module. The degradation characteristics of the experimental facility are analyzed in the course of steady-state operating conditions. Table 3.1. shows the conditions and the results for three working points featuring a constant gas flow rate of 1 l/min.

Table 3.1. Characteristics of three steady-state operating conditions for a gas fow rate of 1 l/min.

Label	c^{g}_{in} /gm^{-3}	SLO /gm^{-2}h^{-1}	c^{g}_{out} /gm^{-3}	c^{abs} /gm^{-3}	c^{mm} /gm^{-3}	SEC /gm^{-2}h^{-1}
1	10 ± 1.1	3.29 ± 0.16	7.14 ± 0.23	7598 ± 50	< 5	0.62 ± 0.25
2	5 ± 0.7	1.64 ± 0.16	2.75 ± 0.19	2719 ± 11	< 5	0.49 ± 0.17
3	2.5 ± 0.6	0.82 ± 0.16	0.86 ± 0.02	1065 ± 36	< 5	0.36 ± 0.12

The surface loads (SLO), based on the membrane area available for absorption, vary between 0.82 and 3.29 g/(m^{2}h), corresponding to toluene inlet concentrations in the gas between 2.5 and 10 g/m^3. The toluene concentrations, measured at the outlet of the reactor, are the measure for the degradation performance. The smaller the toluene inlet surface load the higher the fraction of degraded VOC. The removal efficiency increases from 30 to 65 %. Considerable amounts of toluene can be buffered in the silicone oil. The toluene concentration is by a factor of approximately 1000 higher than in the gas. However, the amount of toluene in the nutrient medium is below the detection limit of 5 g/m3, designating that the bleed stream of the nutrient medium discharges virtually no toluene. The surface elimination capacities (SEC), based on the biofilm area, amount to values of 0.36 to 0.62 g(m^{2}h). These values are comparable to elimination capacities reported for toluene degrading membrane bioreactors (Jacobs *et al*., 2004).

3.2 Buffering of VOC

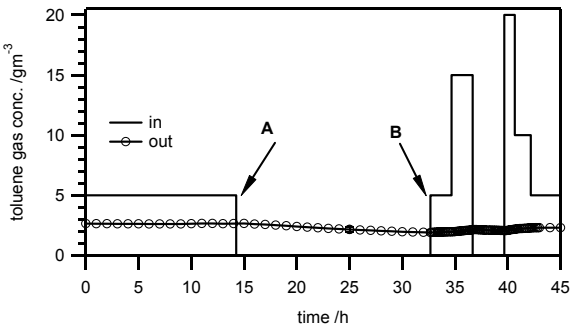

Figure 3. The measured toluene outlet gas concentration for varying inlet loads.

The buffering capacity of the novel set-up is tested by means of feeding fluctuating loads to the reactor and by analyzing the responding toluene concentration in the gas at the reactor outlet. The fluctuating loads are simulated by varying the mass flow rate of toluene for a gas flow rate of 1 l/min.

The solid line represents the inlet gas concentration, the markers the measured outlet toluene concentration. The systematic error of the toluene outlet gas concentration is shown for the data point at 25 h, it is insignificantly small. Starting from the steady-state working point, featuring a toluene inlet concentration of 5 g/m^3, a possible working day in industry, releasing VOC, is simulated. At time A the mass flow rate of toluene is shut down, simulating the beginning of a night. The period featuring no toluene feed lasts for 18 h. At time B the next working day starts. This day is characterized by high, peaking loads and again a period of no toluene feed, *e.g.* lunch time.
The toluene concentration in the outlet stream is virtually constant. This pattern confirms that a buffering of VOC is achieved with the presented system. Although the inlet gas stream features high load fluctuations, the loading of the outlet stream is constant. Assuming that the gas and the absorbent are in equilibrium, this signifies that a big mass of toluene is buffered in the absorbent.

3.3 Prevention from clogging
The distinct data points of the biofilm surface scans are averaged to single values. These single biofilm thicknesses are plotted against the time after inoculation of the reactor. The error bars on the graph represent the standard deviations, which are calculated over the whole area of scanned biofilm.

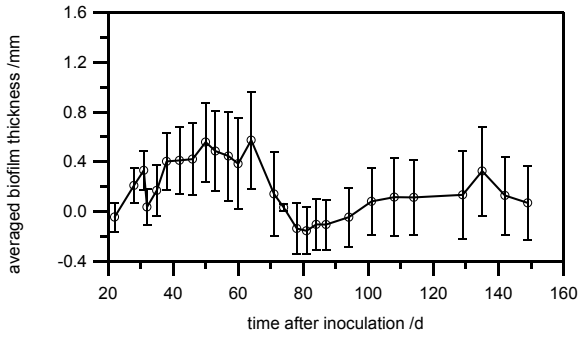

Figure 3. The averaged overall biofilm thickness as a function of time after inoculation.

The course of the averaged biofilm thicknesses shows a considerable variation with time. The bold decrease in thickness after 60 days can be explained with the change in the steady-state toluene feed rate. Up to that point in time, 3.29 g/(m^{2}h) are fed, beyond that time only smaller loads. Some averaged values for the biofilm thickness seem smaller than zero. This fact is explicable by sagging of the membrane. The support structure of the membrane features voids of 5x10 mm^2 between the supportive edges. The small trans-membrane pressure difference, used to press the membrane against the support, suffices to let the membranes sag. However, the calibration of the sensor is made by placing measures of defined thickness on top of the support structure and membrane. Therefore, if the biofilm thickness is small, the averaged thickness may seem negative.
In spite of this vagueness of the absolute thickness measurements it is shown that the biofilm thickness does not exceed an average value of approximately 1 mm.

4 CONCLUSIONS

The novel waste gas treatment system readily degraded poorly water soluble VOC. The degradation capacity was in the same range as those of comparable membrane bioreactors. Fluctuating VOC loads in the waste gas stream were buffered and therewith a constant feed rate for the bacteria was established. The introduction of shear stresses on the biofilm surface showed to remove excessive biomass accumulations and to prevent the reactor from clogging.

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