

# Removal of dimethylsulfide, n-hexane and toluene from waste air in a flat membrane bioreactor under continuous conditions

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## Abstract

Dimethylsulfide (DMS), n-hexane and toluene removal from a waste air was carried out by using a flat composite membrane bioreactor under continuous feeding conditions. The composite membrane consisted of a dense polydimethylsiloxane top layer with an average thickness of 1.5  $\mu\text{m}$  supported with a porous polyacrylonitrile layer of 50  $\mu\text{m}$ . The membrane bioreactor (MBR) was operated during 9 months in which several operational conditions were applied. The inlet load of each compound ranged from 0 to 350  $\text{g m}^{-3} \text{h}^{-1}$  and removal efficiencies of 80, 70 and 0 to 30 % were reached for DMS, toluene and hexane respectively. Two different empty bed residence time (EBRT) were applied on the MBR in order to check the influence of the residence time on the reactor performance. In this case, DMS and toluene removal increased with an increasing EBRT, while the removal of hexane remained constant. By increasing the flow rate of the recirculated liquid from 22  $\text{l min}^{-1}$  to 45  $\text{l min}^{-1}$ , the total performance of the biofilter decreased. To increase the mass transfer of hexane in order to get a higher removal, an emulsion of water/silicone oil 80/20 V% was used as recirculated medium at the liquid side of the reactor. This caused a decrease in DMS removal while the removal of toluene remained constant. The variation on the hexane removal decreased significantly, so the reactor became more reliable for degrading hexane,

**Keywords:** biofiltration of waste gases; membranes; pollution control; volatile organic compounds; environmental biotechnology

## INTRODUCTION

For the control of volatile organic compound (VOC) emissions, biological gas treatment techniques have been studied and used as alternatives for the traditional physical-chemical techniques. Using a membrane bioreactor (MBR) for waste gas treatment has the technological advantage that it is possible to separate the gas and liquid phases. In this way the conditions of both phases can be optimized much more easily. Pollutants diffuse through the membrane and are subsequently degraded by the microorganisms in the biofilm which is attached onto the membrane. A MBR could potentially be more effective than conventional biosystems, although it still requires additional investigation and optimization with other compounds and with complex VOC mixtures. This study was performed to evaluate the performance of a MBR to treat a waste gas contaminated with a 1:1:1 (wt) mixture of dimethylsulfide (DMS), n-hexane and toluene under various operating conditions and to determine if hexane removal could be improved by using a water/silicone oil (80/20 V%) emulsion at the liquid side of the reactor.

## MATERIALS AND METHODS

### Membrane bioreactor system

A commercially available flat composite membrane (GKSS Forschungszentrum Geesthacht, Germany) consisting of a porous polyacrylonitrile support layer, 50  $\mu\text{m}$ , and coated with a very thin dense polydimethylsiloxane top layer, 1.5  $\mu\text{m}$ , was used. An overview of the reactor set-up can be found in Fig. 1. The MBR which consisted of two identical compartments made of Perspex, was placed in an isothermal chamber at 23  $^{\circ}\text{C}$ . Each compartment of the reactor had four channels with a length of 20 cm, a width of 5 mm and a depth of 2 mm. The membrane was clamped between the two compartments, resulting in a contact area of 40  $\text{cm}^2$ . Dry air was polluted with the VOC mixture by using a syringe pump (New Era, infusion/withdraw NE 1000 model, USA) and was flowing along the porous side of the membrane. The air flow was adjusted by using a mass flow controller (Brooks Instruments, USA) and was introduced countercurrent with the recirculation liquid, which was adjusted by a membrane pump (LMI, Milton Roy, USA). The recirculation bottle was placed in a thermostatic water bath at 23  $^{\circ}\text{C}$  and stirred at 500 rpm (IKA RCT basic, Germany).

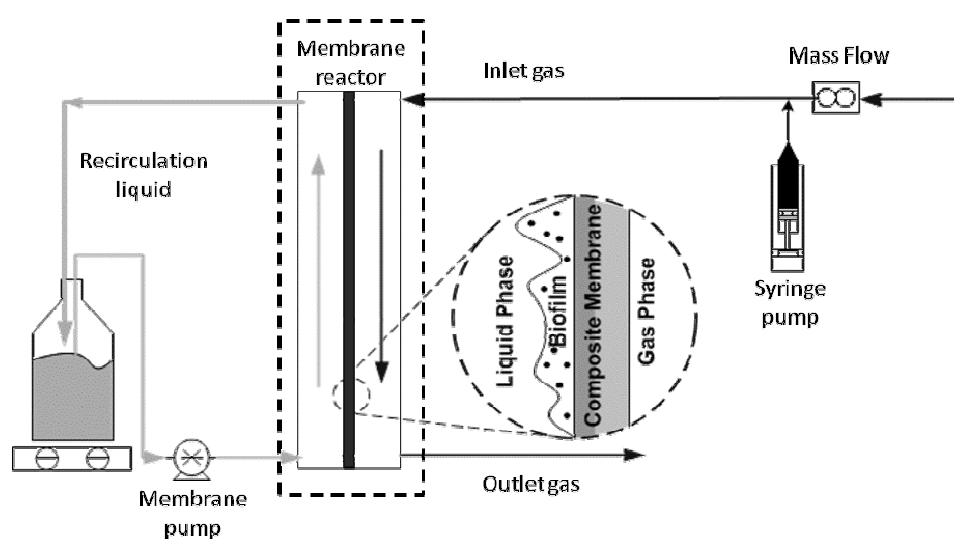


Fig. 1. Schematic diagram of the flat sheet membrane bioreactor<sup>[1]</sup>.

The necessary macro and micronutrients were incorporated using a pH buffered nutrient solution (pH 7) containing  $\text{KNO}_3$ , 10.7  $\text{g L}^{-1}$ ,  $\text{KH}_2\text{PO}_4$ , 3.0  $\text{g L}^{-1}$ ,  $\text{K}_2\text{HPO}_4$ , 3.0  $\text{g L}^{-1}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.5  $\text{g L}^{-1}$ , P, Ca, Fe, Zn, Co, Mn, Mo, Ni, B and vitamins at trace doses. The volume of nutrients added was kept at a C:N:P ratio of 100:5:1<sup>[2]</sup>. This ratio was weekly checked by measuring the nutrients in the leachate. The MBR was inoculated with a mixed microbial culture obtained from an activated sludge (Ossemeersen WWTP, Ghent) and was first preadapted during 30 days with the compounds to be treated to acclimate the mix of microbes in the sludge. Inoculation of the MBR occurred by recirculating 500 ml of the preadapted activated sludge the dense side of the membrane, during 24 hours. In this period a biofilm could be formed upon the surface of the membrane.

### Process conditions

The membrane bioreactor was operated under continuous loading for 9 months. During this period several operational conditions were tested. DMS, n-hexane and toluene concentrations were varied from 0.2 to 2.5  $\text{g m}^{-3}$  at gas empty bed residence times (EBRT) of 20 and 30 s. At the liquid side, the flow rate was changed from 22  $\text{ml min}^{-1}$  to 45  $\text{ml min}^{-1}$ . Finally the water at the liquid side was replaced by an emulsion of water with silicone oil in an 80/20 V% ratio.

During these experiments the inlet and outlet concentrations were measured as well as the CO<sub>2</sub> production at the outlet of the membrane.

To determine the mass transfer of the different compounds through the membrane<sup>[3,4]</sup>, the bioreactor was operated during 1 week without liquid recirculation at the liquid side of the reactor. In the last 2 months of the experimental study, the water/silicone V% ratio was adjusted and the biomass was removed in order to determine the influence of the liquid on the mass transfer of the different compounds. An overview of the applied operational parameters can be found in table 1.

**Table 1.** Operational parameters for Membrane biofilter experiments

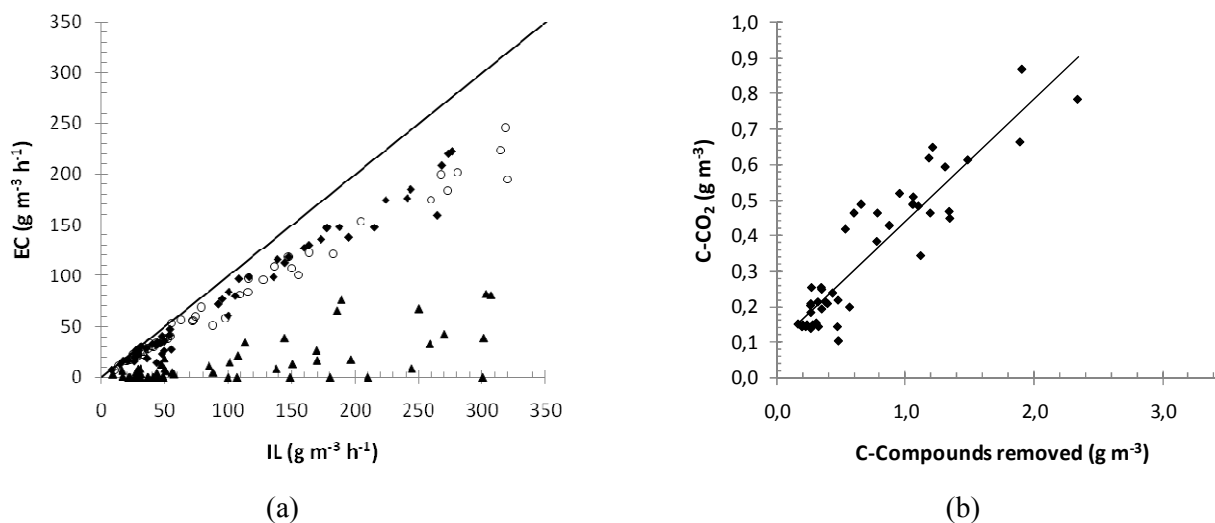
Day	inlet concentration (g m <sup>-3</sup> )	EBRT (s)	Liquid flow (ml min <sup>-1</sup> )	liquid
0 - 113	0 - 2.5	30	22	100 V% water + Biomass
114 - 190	0 - 1.9	20	22	100 V% water + Biomass
190 - 211	0-0.9	20	45	100 V% water + Biomass
212 - 270	0 - 1.15	30	22	80/20 V% water/oil + Biomass
270 - 277	0 - 2.9	30	22	No liquid (air)
278 - 297	0 - 2.9	30	22	100/0 V% water/oil + No Biomass
298 - 303	0 - 2.9	30	22	80/20 V% water/oil + No Biomass
304 - 311	0 - 2.9	30	22	60/40 V% water/oil + No Biomass
312 - 323	0 - 2.9	30	22	40/60 V% water/oil + No Biomass

### Analytical techniques

The gas concentrations of the different compounds in the gas flow were monitored daily by taking gas samples of 500 µl using a 1.0 ml GASTIGHT<sup>®</sup> syringe at the gas inlet and outlet of the reactor. Analysis of these samples were performed by using a FID gas chromatograph (4890D Series, Agilent Technologies, USA) equipped with an HP-5 capillary column (15 m × 0.53 mm × 1.5 µm, Agilent Technologies, USA) and He as carrier gas used at a flow-rate of 2 ml min<sup>-1</sup>. The CO<sub>2</sub> gas concentration at the outlet was determined by using a CARBOCAP<sup>®</sup> carbon dioxide analyser (GM70 model, Vaisala, Finland).

## RESULTS AND DISCUSSION

### Performance of the Membrane bioreactor



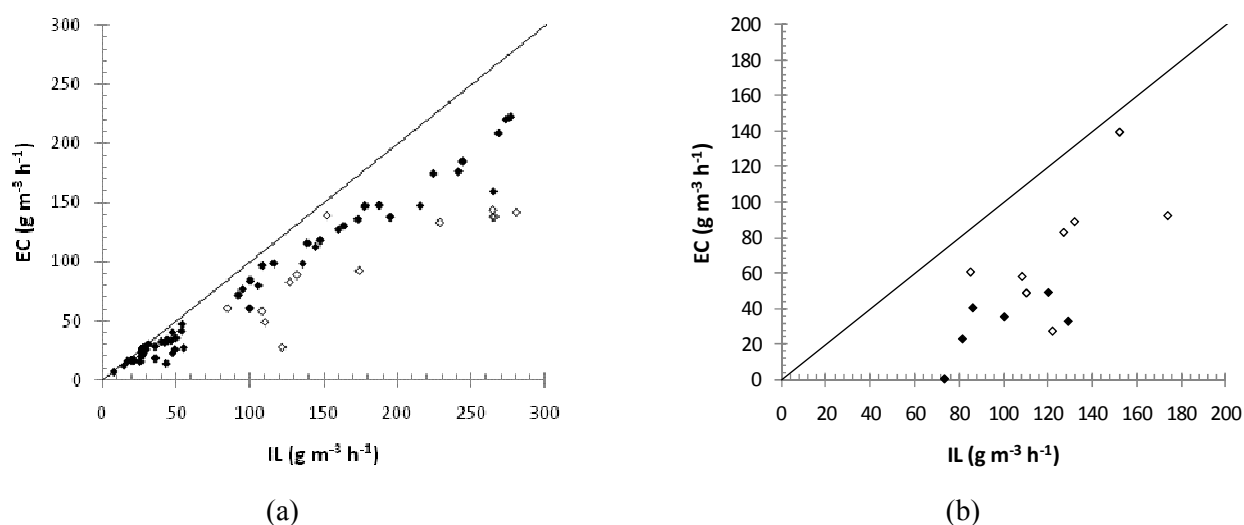
**Fig. 2.** (a) Elimination Capacity vs. Inlet Load for (◆) DMS; (○) Toluene and (▲) Hexane at an EBRT of 30 s and water as liquid medium.

(b) Carbon formed as CO<sub>2</sub> vs. carbon removed by eliminating the compounds.

To evaluate the performance of the MBR, the Inlet Load (IL), Elimination Capacity (EC) and Removal Efficiency (RE) were monitored daily. Plotting the EC of the different compounds in function of the IL, both expressed in g compound per reactor volume (m<sup>3</sup>) and per hour, see Fig. 2(a), shows that the biodegradation of DMS and toluene are quite similar, while the removal of hexane is significant lower. RE of more than 80 % were reached for DMS at IL up to 275 g m<sup>-3</sup> h<sup>-1</sup> and an EBRT of 30 s. For toluene the RE were slightly lower at these high IL, but still reached 70 % at IL up to 320 g m<sup>-3</sup> h<sup>-1</sup>. For hexane the RE was less stable and varied from 0 to 30 % and this for the complete range of the measured IL.

A linear relationship was found between, the amount of Carbon-CO<sub>2</sub> which is formed and the amount of the Carbon which is removed by eliminating the compounds, see Fig. 2(b), indicating that the removal of the compounds is due to biodegradation. Linear regression resulted in a value of  $0.34 \pm 0.02$  g m<sup>-3</sup> of C-CO<sub>2</sub> which is formed out of each g m<sup>-3</sup> of C-Compounds removed. This means that at least 34 % of the C is incorporated in CO<sub>2</sub>. The other 74 % of C will probably be incorporated in additional biomass, as dissolved carbon in the recirculated medium or escaping as CO<sub>2</sub> along the headspace of the liquid medium. To ensure that no compounds were escaping along the headspace of the liquid medium, a gas sample of the headspace was analysed daily, but no compounds were retrieved.

### Influence of EBRT and liquid flow rate



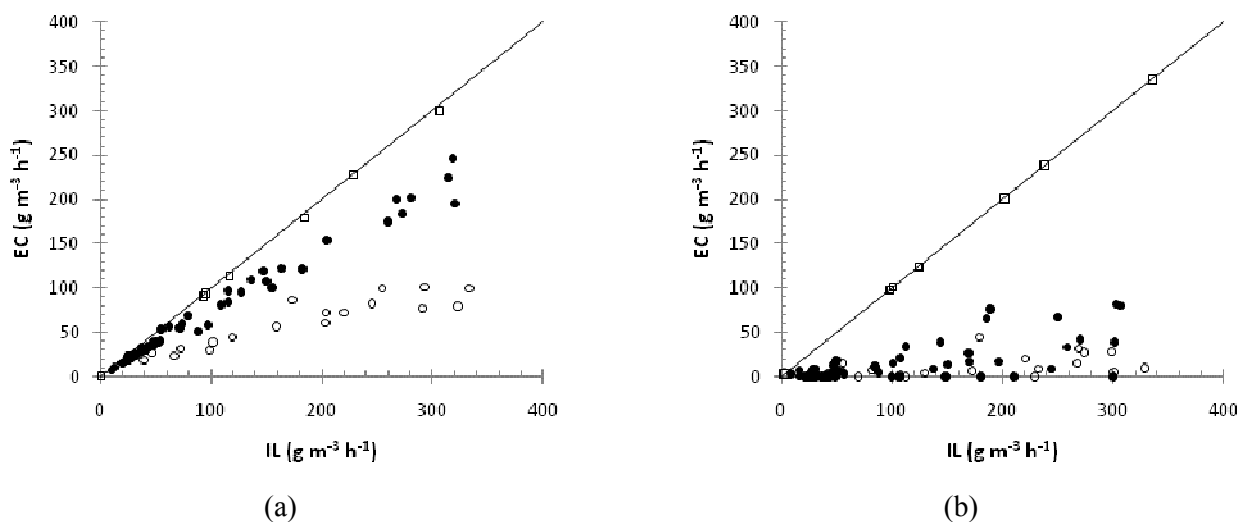
**Fig. 3.** (a) Elimination Capacity vs. Inlet Load for DMS at an EBRT of (◆) 30 s and (◇) 20 s with water as liquid medium.

(b) Elimination Capacity vs. Inlet Load for DMS with a liquid flow rate of (◇) 22 ml min<sup>-1</sup> and (◆) 45 ml min<sup>-1</sup> at an EBRT of 20 s and with water as liquid medium.

Lowering the EBRT from 30 s to 20 s, did influence the performance of the reactor slightly in the measured range of IL. The lower EBRT had the highest impact on the DMS degradation, see Fig. 3(a). In this case the RE lowered from 80 %, for IL up to 160 g m<sup>-3</sup> h<sup>-1</sup>, to 50 % for IL ranging from 220 to 280 g m<sup>-3</sup> h<sup>-1</sup>. For toluene there was no significant change in performance for IL up to 300 g m<sup>-3</sup> h<sup>-1</sup> and RE of 70 % were still reached. At higher IL (300 g m<sup>-3</sup> h<sup>-1</sup> < IL < 350 g m<sup>-3</sup> h<sup>-1</sup>) the RE dropped to 50 % at an EBRT of 20 s, while this stayed around 70 % at an EBRT of 30 s. In case of hexane, the lower EBRT did not affect the performance of the MBR and RE still varied between 0 and 30 % for IL ranging from 8 to 305 g m<sup>-3</sup> h<sup>-1</sup>.

Increasing the flow rate of the liquid medium from  $22 \text{ ml min}^{-1}$  to  $45 \text{ ml min}^{-1}$  at the dense side of the membrane decreased the performance of the reactor for the removal of DMS, see Fig. 3(b) and for toluene. At a liquid flow rate of  $22 \text{ ml min}^{-1}$  and an EBRT of 20 s, the RE for DMS was around 80 % for IL ranging between 60 and  $140 \text{ g m}^{-3} \text{ h}^{-1}$ , while the RE decreased to values around 30 %, when increasing the liquid flow rate up to  $45 \text{ ml min}^{-1}$ . For toluene the RE decreased from 70 % to 40 %. A possible explanation could be found in the fact that at higher liquid flow rates, more biomass will be swept away by the liquid, decreasing the thickness of the biofilm attached at the dense side of the membrane.

### Mass transfer resistance



**Fig. 4.** (a) Elimination Capacity vs. Inlet Load for toluene with (□) air; (●) water with biomass and (○) water without biomass as liquid medium, EBRT = 30 s.  
(b) Elimination Capacity vs. Inlet Load for hexane with (□) air; (●) water with biomass and (○) water without biomass as liquid medium, EBRT = 30 s.

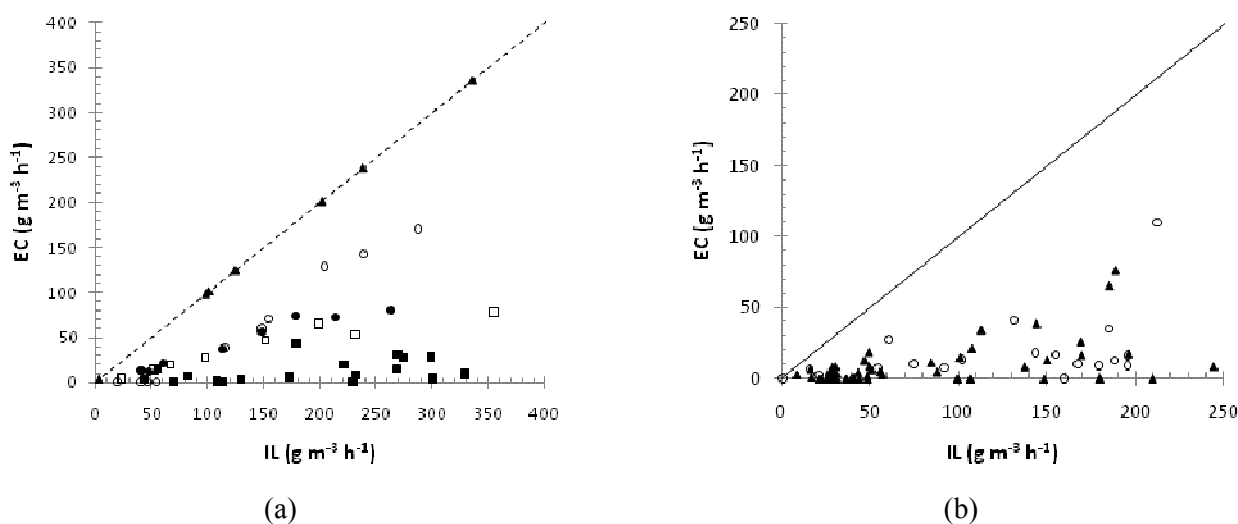
Nevertheless a hydrophobic membrane was used; the results show that the removal of the hydrophobic compound hexane remained very low (RE < 30 %), see Fig. 4(b). In order to determine the mass transport for the three compounds, the liquid medium was replaced by non-polluted air and the inlet and outlet concentration at the gas side of the reactor were monitored, while increasing the inlet concentration daily. When plotting the apparent EC in function of the IL for the different compounds, it was clear that the membrane itself did not provide any mass transfer resistance for the different compounds to move from one compartment to the other and this for IL up to  $350 \text{ g m}^{-3} \text{ h}^{-1}$ , see Fig. 4. If the air at the liquid side was replaced by distilled water (no biomass), it became clear that the addition of a water layer, increased the mass transfer resistance significantly. In the case of toluene the apparent RE decreased from 100 % to 35 %, when the air was replaced by distilled water, for IL up to  $300 \text{ g m}^{-3} \text{ h}^{-1}$ , see Fig. 4(a). Also for DMS a decrease from 100 % to 35 % was visible. For hexane, see Fig. 4(b), the presence of water at the liquid side had the highest influence. In this case, the apparent RE dropped from 100 % to a RE which varied between 0 and 10 %. These results illustrate that the low biodegradation of hexane, which has a high Henry coefficient, is probably due to the high transfer resistance caused by the water layer.

### Water/oil emulsion

In order to decrease the mass transfer resistance for hexane, an emulsion of water and silicone oil was used at the liquid side of the reactor. When increasing the amount of silicone oil, the mass transfer of hexane from the gas to the liquid side increased, see Fig. 5(a). The apparent RE of hexane increases from 0 – 10 % to 25, 35 and up to 60 % by using a water/silicone oil

emulsion of respectively 80/20, 60/40 or 40/60 V%. Using the water/oil emulsion at the liquid side of the reactor did not affect the mass transfer of the DMS and even increased the mass transfer of toluene.

Using a water/silicone oil 80/20 V% emulsion inoculated with biomass at the liquid side of the reactor, resulted in a more stable but still very low RE for hexane, RE = 10 %, see Fig. 5(b). An even higher RE of hexane, could probably be reached by increasing the amount of silicone oil at the liquid side of the reactor, but one has to be careful not to increase the amount of silicone oil too much, as the bacteria live in the water and at the surface of the silicone oil and water. By increasing the amount of oil too much, the contact area between the oil and water will decrease, resulting in a lower biodegradation, so more research has to be done to find the optimal ratio between the water and silicone oil. For toluene the RE remained stable when using a water/silicone oil emulsion of 80/20 V% inoculated with biomass at the liquid side of the reactor. In this case RE of 70 % were reached for IL even up to 350  $\text{g m}^{-3} \text{h}^{-1}$ . In case of DMS the RE decreased from 80 to 40 %.



**Fig. 5.** (a) Elimination Capacity vs. Inlet Load for hexane with (▲) air; (○) 40/60 V%; (●) 60/40 V%; (□) 80/20 V%; (■) 100/0 V% water/silicone oil emulsion as liquid medium (without biomass), EBRT = 30 s.

(b) Elimination Capacity vs. Inlet Load for hexane with (▲) water and (○) an 80/20 V% water/silicone oil emulsion as liquid medium (with biomass), EBRT = 30 s.

## CONCLUSIONS

This research illustrates the treatment of a waste gas polluted with a DMS, n-hexane and toluene mixture by a lab-scale membrane bioreactor under continuous loading conditions. Elimination capacities of 245 (RE = 70 %) and 222 (RE = 80 %)  $\text{g m}^{-3} \text{h}^{-1}$  were reached for IL up to 320 and 280  $\text{g m}^{-3} \text{h}^{-1}$  for toluene and DMS respectively, while the elimination capacity of hexane varied between 0 and 80  $\text{g m}^{-3} \text{h}^{-1}$  (RE = 0 – 30 %) for IL up to 310  $\text{g m}^{-3} \text{h}^{-1}$  and this at an EBRT of 30 s. The low removal of hexane is probably caused by the high mass transfer resistance for hexane, due to the presence of water at the liquid side of the reactor. Decreasing the EBRT from 30 s to 20 s, decreases the RE for toluene and DMS at IL higher than respectively 300 and 220  $\text{g m}^{-3} \text{h}^{-1}$ , while the RE of hexane remained constant. Increasing the liquid flow rate from 22 to 45  $\text{ml min}^{-1}$ , led to a decrease in the performance of the membrane bioreactor. By using a water/silicone oil 80/20 V% emulsions instead of water at the liquid side, the removal of toluene remained constant, while the removal of DMS decreased from 80 to 40 %. The removal of

hexane became more stable and so much more reliable. A higher hexane removal can probably be reached by changing the water/silicone oil ratio, but further research is required.

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