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# Two phase partitioning membrane bioreactor: A novel biotechnique for the removal of dimethyl sulphide, n-hexane and toluene from waste air

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## HIGHLIGHTS

- Increasing Henry coefficient decreases the removal efficiency in a MBR.
- A TPPMB combines a two phase partitioning reactor with a membrane bioreactor.
- A TPPMB is reliable to treat a mixture of hydrophobic and hydrophilic compounds.

## ARTICLE INFO

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## ABSTRACT

This study is a comparative study between a flat sheet composite membrane bioreactor (MBR) and a new type of MBR, the two phase partitioning membrane bioreactor (TPPMB) to examine the merits of using silicone oil to improve the mass transfer in a membrane type bioreactor. Dimethyl sulphide (DMS), n-hexane and toluene removal from a waste air was carried out by a MBR under continuous feeding conditions. The performance of this reactor was compared with the performance of a TPPMB. In the TPPMB a 60/40 V% water/silicone oil emulsion inoculated with activated sludge was used as recirculation liquid in order to reach an acceptable removal for both hydrophobic and hydrophilic compounds. Removal efficiencies (RE) of respectively 76.8 ± 7.7, 77.6 ± 13.0 and 12.1 ± 12.3% were reached for toluene, DMS and hexane inlet concentrations ranging up to 2.6 g $m^{-3}$ for each compound (Inlet load (IL) $\leqslant$312 g $m^{-3}$ $h^{-1}$) in a MBR. This indicates that a MBR is suitable to treat DMS and toluene, but unreliable to treat hexane. In a TPPMB RE of 85 ± 5, 62 ± 5 and 53 ± 6% were reached for toluene, DMS and hexane inlet concentrations ranging up to 2.8 g $m^{-3}$ for each compound (IL $\leqslant$ 336 g $m^{-3}$ $h^{-1}$) respectively. The RE for hexane is significantly higher in a TPPMB, while the variability of the hexane removal decreased, so the TPPMB is suitable and more reliable for degrading hexane than a MBR. The increase in RE of hexane and toluene can be related to the increase in transfer when applying 40 V% silicone oil.

## 1. Introduction

For the control of volatile organic compound (VOC) emissions, biological gas treatment techniques such as biofiltration, biotrickling filtration and bioscrubbing have been studied and used as alternatives for the traditional physical–chemical techniques [1–5]. A newer biotechnique for the treatment of complex emissions is the use of a membrane bioreactor (MBR).

The last two decades there has been a significant growth in the industrial applications of membrane technology. Membrane systems are now available in several different forms and sizes and can be used for a number of different, very characteristic separation processes. Some of the advantages of this separation system over the traditional techniques are the small foot print, the selectivity towards the process and the use of one universal design for all different situations. The application of membrane bioreactors for air treatment is gaining more interest and different bioreactor configurations have already been used at laboratory scale. [6–11]. The choice of the applied module configuration depends generally on economics, compactness of the system and ease of operation,

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cleaning and maintenance. A flat sheet membrane has a low packing density (<100–400 $m^2\ m^{-3}$), but has a low fouling tendency and is easy to clean, while a hollow fibre membrane has a very high packing density (<30,000 $m^2\ m^{-3}$), but has a very high fouling tendency and is very hard to clean.

In a MBR used for air treatment, the liquid side of the reactor will be separated from the gas side by using a porous, dense or composite (porous part in combination with a dense part) membrane. At the liquid side of the membrane bioreactor an aqueous phase containing nutrients and inoculated with microorganisms is recirculated continuously. At the gas side a polluted air stream is fed to the reactor and the gaseous pollutants will diffuse through the membrane, where they will be degraded by the biofilm attached on the membrane surface or by the microorganisms in suspension. The flux of the different pollutants over the membrane can be described by Eq. (1), with $F$ the mass flux of the compound through the membrane ($g\ s^{-1}$), $K_{ov}$ the overall mass transfer coefficient ($m\ s^{-1}$), A the membrane surface area ($m^2$), $H$ the dimensionless air–water partition coefficient or Henry coefficient ($g\ m^{-3}/g\ m^{-3}$) and $c_g$ and $c_l$ respectively the concentration in the gas and liquid phase [12].

$$F = K_{ov} \cdot A \cdot \left(\frac{c_g}{H} - c_l\right) \tag{1}$$

In this case, the driving force for the compounds to diffuse through the membrane is based on a concentration gradient between the liquid phase and the gas phase. This driving force highly depends on the air–liquid partitioning coefficient of the pollutant. The driving force for a pollutant with a low $H$ value will be higher than the driving force for a compound with a high $H$ value. Also the microbial activity will influence the driving force, as $c_l$ decreases with increasing bioactivity. The overall mass transfer resistance, $1/K_{ov}$, is a combination of the resistance in the gas phase, membrane, biofilm and liquid phase [13].

The main advantage of a membrane bioreactor is the easy way to control the microbial degradation process (pH, nutrients, temperature), due to the continuous recirculation of the aqueous phase and the independent control of gas and liquid phase. Other advantages are the high specific surface area, the low pressure drop and the absence of preferential flowing. The high selectivity of the membrane material can enhance the potential to eliminate VOC characterised by poor water solubility, by lack of biodegradability and by toxicity [12]. Some hydrophilic membrane materials such as polydimethylsiloxane (PDMS) or polyolefin can increase the mass transfer of poorly water soluble compounds. Possible disadvantages of a membrane bioreactor are the high investment costs, the additional mass transfer resistance caused by the membrane, a decreased biofilm activity as the biofilm ages and clumping and clogging of hollow fibre membranes at high biofilm growth.

Different lab-scale studies have already indicated the good performance of a MBR for the biodegradation of a wide range of single VOC with different hydrophobicity [14], but studies on the performance of a MBR for the removal of mixtures is scarce. A MBR could potentially be more effective than conventional biosystems, although it still requires additional investigation and optimisation with other compounds and with complex VOC mixtures. Until now only a mineral medium largely consisting out of water was used at the liquid side of the membrane. In air fed bioreactors the overall volumetric mass transfer from the gas phase to the liquid phase is proportional to the solubility of the contaminant in the liquid phase [15,16]. The water at the liquid side of the membrane can therefore significantly decrease the mass transfer of hydrophobic compounds, e.g. hexane, reducing the removal capacity of the reactor.

**Table 1**
Compound properties.

| Compound | DMS | Hexane | Toluene |
|---|---|---|---|
| Group | Sulphide | Alkane | Aromatic |
| Solubility in $H_2O$ at 25 °C ($g\ L^{-1}$) | 45[a] | 0.016[a] | 0.32[a] |
| Vapour pressure at 25 °C (mmHg) | 647[a] | 151[a] | 27.7[a] |
| Henry coefficient[b] (-) ($c_g/c_l$) | 0.048 | 44 | 0.43 |

[a] SciFinder. http://scifinder.cas.org. Last accessed on 28-11-2013.
[b] Calculated using the solubility and the vapour pressure, which is valid for diluted solutions at low pressures (<20 bar; ideal gas phase can be assumed).

This research is a two part study examining the performance of composite flat sheet MBR, before and after the addition of silicone oil to the mineral medium. By adding a liquid organic phase, e.g. silicone oil, as mass transfer vector for hydrophobic compounds, the performance of a MBR to treat hydrophobic compounds can be optimised [16]. The first part of 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 dimethyl sulphide (DMS), n-hexane and toluene under various operating conditions, with inlet concentration ranging up to 3.6 $g\ m^{-3}$ per compound. DMS, hexane and toluene are VOC which are often found in waste gases of industrial sources, but with different physical properties. Especially the difference in water solubility is remarkable, see Table 1.

DMS is known to have a very high solubility in water (low Henry coefficient), but bacterial cultures responsible for the degradation of this compound are known to be slow growers, e.g. *Hyphomicrobium* has a specific growth rate of only 0.089 ± 0.022 $h^{-1}$ at pH 7 and with $KNO_3$ as nitrogen source [17]. Hexane has the highest Henry coefficient and is the least soluble in water, while toluene is a VOC with a Henry coefficient which is about 10 times higher than the one of DMS and about 100 times lower than the one of hexane. This Henry coefficient is a very important characteristic which affects the performance of the reactor, as it influences the overall volumetric mass transfer rate from the gas phase to the aqueous phase [16]. Since the biofilm is composed of more than 90% water, the mass transfer from the gas phase, through the membrane into the biofilm can be rate limiting [18], especially when treating poor water soluble VOC (high Henry law coefficient).

In order to improve the mass transfer of more hydrophobic compounds, e.g. hexane, the mineral medium at the dense side of the membrane was replaced by a water/silicone oil emulsion in a second part of this research. Using a water/silicone oil emulsion inoculated with sludge to remove VOC from a waste air stream has previously been successfully applied in bioreactors of various configurations [19–22], but has never been applied as such in a membrane bioreactor. Therefore the second part of this research was set up to compare the performance of a more conventional MBR with the performance of a novel biotechnique, i.e., a two phase partitioning membrane bioreactor (TPPMB). In order to reach a sufficient mass transfer for hydrophobic, as for hydrophilic compounds, an optimal ratio between the water and the silicone oil was first determined. Using this optimal ratio, the TPPMB was first fed with a waste air stream only contaminated with hexane. Afterwards a mixture of 1:1:1 (wt) DMS, n-hexane and toluene was fed to the TPPMB in order to examine the performance of the reactor on the removal of a mixture of compounds with varying solubilities.

## 2. Materials and methods

### 2.1. Membrane bioreactor system

A commercially available flat composite membrane (GKSS Forschungszentrum Geesthacht, Germany) consisting of a porous polyacrylonitrile support layer, 50 μm, and coated with a very thin dense polydimethylsiloxane (PDMS) top layer, 1.5 μm, was used.