

Biological Waste Gas Purification using Membranes: Opportunities and Challenges

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1 INTRODUCTION

Biotechnology to purify air and waste gasses has been applied more frequently in recent years, because they eliminate many of the drawbacks of classical physical-chemical techniques (Kennes and Veiga 2001, Shareefdeen and Singh, 2005). The disadvantages of the traditional air-treatment techniques are high-energy costs (incinerators), the use of chemicals (chemical scrubbers) and the production of waste products (incinerators, scrubbers, activated carbon filters). Biological waste gas purification is a 'green' technology that requires only minimal energy inputs and produces little to no waste. Biological waste gas purification is safe as it is operated at ambient temperatures without the requirement of storage and handling of chemicals and is often applied because of its low operational costs.

However, biological waste gas purification is still relatively new in many application fields. For example, applications of biological waste gas treatment for high contaminant concentrations are still scarce at this moment. The main reason is that biological treatment systems face operational limitations for the treatment of high contaminant concentrations as it may lead to biomass clogging inside the biological treatment system. Biomass clogging will result in poor airflow distribution, high pressure drop over the system and unstable operation, that eventually will lead to a reduction of performance. This severely limits the applicability of conventional biofiltration systems for the treatment of airstreams with high contaminant concentrations. Traditional technologies like incineration are commonly used to treat waste gases with high concentrations of contaminants. This is attractive when the concentrations are high enough to thermodynamically support burning the contaminants without additional fuel. If this is not the case, incineration is relatively expensive because of the additional fuel requirement. The cost of operating an

incinerator is then directly related to the energy prices, which have been increasing significantly over the last couple of years.

Conventional biofiltration systems can have limitations in terms of process control, and often higher degradation capacities or smaller footprints are required. Bioreactors using membranes are of interest for new applications as they have some important advantages over conventional biofiltration systems. The first advantage is that any biomass accumulation does not interfere with the gas phase and that biomass accumulation can be better controlled. Secondly, it eliminates the risk of unintentionally drying out of the biofilm and ensures a sustainable control of moisture, which is often a problem in the operation of conventional biofilters. Another advantage is the improved homogenous airflow distribution as well as better controlled nutrient addition to the biofilm. Finally, poor water-soluble compounds with high membrane permeability can be treated effectively with membrane bioreactors as has been demonstrated for hexane (Reiser, 1994). The membrane separates the gas phase from the liquid phase holding the biology, which improves the possibilities to control and optimize the biological process.

This paper describes reactor design considerations of membrane bioreactor for waste gas treatment. Current limitations and challenges for further development of applications are discussed including some possible interesting application fields.

2 PROCESS MECHANISM OF A MEMBRANE BIOREACTOR

In a membrane bioreactor for gas treatment, the membrane is the interface between the contaminated gas phase and a liquid phase containing nutrients. The pollutants diffuse from the waste gas through the membrane to the biofilm that is attached on the membrane at the liquid membrane interface. The micro-organisms in the biofilm will obtain oxygen from the gas phase, while the nutrients are obtained from the liquid phase. The liquid with the nutrients is usually recirculated, buffered to sustain a suitable pH and refreshed occasionally to add nutrients or remove degradation products.

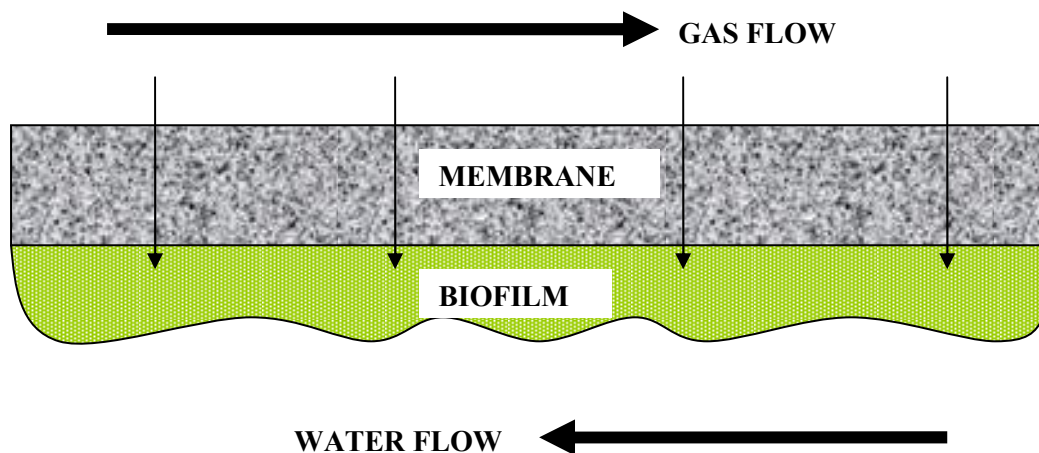


Figure 1: Process flows in a membrane bioreactor

A membrane bioreactor will have an overall mass transfer coefficient K_{ov} ($m\ s^{-1}$) that is defined by the mass transfer coefficient on the gas phase side of the membrane k_g , the mass transfer coefficient for the membrane k_m , and the mass transfer in the liquid phase k_l as written as

$$1/K_{ov} = 1/k_g + 1/k_m + 1/k_l \quad (1)$$

The mass of pollutants transferred through the membrane, the flux J ($g\ m^{-2}\ s^{-1}$), is an important design parameter for membrane bioreactors and is defined as the overall mass transfer multiplied by the concentration gradient dC ($g\ m^{-3}$).

$$J = K_{ov} * dC \quad (2)$$

The mass transfer coefficient for pollutants in the membrane k_m is defined as the ratio of the permeability of the pollutant P ($m^2\ s^{-1}$) in the membrane and the membrane thickness d (m). Permeability has been described by Solubility of the air/membrane partition coefficient S ($g\ m^{-3}_{membrane} / g\ m^{-3}_{air}$) multiplied by the diffusion coefficient D_m through the membrane material (Mulder, 1996).

$$K_m = P / d = (S * D_m) / d \quad (3)$$

There are two basic types of membrane that are used in biological waste gas purification: micro-porous membranes and dense-phase membranes. High membrane permeability for the pollutants is an important factor in choosing a membrane type or membrane material for a specific application.

3 DESIGN CONSIDERATIONS

3.1 Introduction

Membrane bioreactors for waste gas treatment are relatively new. Suitable membrane material and reactor configuration are essential in the further development and successful application of membrane bioreactors for waste gas purification. The relatively high cost of the membrane materials, and the lack of experience with the different types of membranes and possible reactor configurations on a wide range of pollutants have been an important limitation to the advancement of membrane bioreactors. Membrane biotechnology has evolved over the last couple of years in other areas like industrial and municipal wastewater treatment and creates new possibilities for biological waste gas treatment.

3.2 Types of Membrane

There are basically two membrane types: micro-porous membranes and dense-phase membranes. Micro-porous membranes have a porous structure with a porosity of up to 30-85% (Hartmans *et al.*, 1992). The pollutants can cross the membrane by diffusing through the gas-filled pores, yet the pores are small enough to prevent micro-organisms to pass the membrane. The membrane material is often chosen for having hydrophobic properties, so that at relatively low trans-membrane pressures the risk of water penetration is reduced. Dense-phase membranes have no macroscopic pores meaning that the pollutant has to diffuse through the membrane material. This imparts some potential for contaminant selectivity when choosing a type of dense-phase membrane. It is critical that a membrane material with a high gas diffusion

coefficient should be used for the specific contaminants to minimise the mass transfer resistance of the dense-phase membrane applied.

In theory, micro-porous membranes have significantly lower mass transfer resistance than dense-phase membranes. Micro-porous membranes have higher permeability and a poor to no selectivity in permeation compared to dense-phase membranes. However, at high air pressures, systems deploying micro-porous membranes run the risk of trans-membrane gas flow, which may compromise the integrity of the membrane. In addition, micro-porous membranes are not a complete definite barrier for micro-organisms, which eliminates important advantages for certain applications. Furthermore, micro-porous membranes are subject to fouling due to blocking of the micro-pores, leading to a decline in performance over time (van Reij 1996 en de Bo 2003). Dense-phase membranes seem therefore, in principal, more suitable than micro-porous membranes for long term sustainable operation. Since the contaminant may actually dissolve into the membrane material, the polymer phase of dense-phase membranes might also act as a buffering medium for fluctuating inlet pollutant loads.

To combine the best characteristics of both types of membranes, composite membranes made of micro-porous membrane supports coated with a dense-phase polymer layer have been studied (de Bo *et al.*, 2003) and seem very promising. The very thin layer of dense-phase membrane is located on the liquid side. The supporting porous layer is located on the gas-phase side. The composite membranes will be inherently more complex and more expensive to manufacture than the dense-phase or the micro-porous membranes.

The choice of membrane material depends on the pollutants to be treated. Different membrane materials have been studied for gas treatment as has been illustrated by Fitch (Fitch, 2005). Examples of membrane materials are poly(butadiene), latex, poly(vinylalcohol), poly(sulfone), poly(styrenesulfone), poly(amide), poly(ethylene), poly(tetrafluoethene), poly(propylene) and poly(dimethylsiloxane). Different membranes are commercially available as they have been successfully used in areas such as the medical and the food processing fields. The polymer selection for the dense-phase membrane material needs to have a high solubility for the pollutant. Otherwise, mass transfer resistance across the membrane will hinder the rate of biodegradation. Poly(dimethylsiloxane) (PDMS) dense-phase membranes are relatively permeable and seems to be relatively unselective towards pollutants (Merkel *et al.*, 2000 and De Bo *et al.*, 2003). The risk of dense phase membrane failures due to dissolution or swelling of polymer when solubility is extremely high should be avoided. The effect has been demonstrated in membrane bioreactors for benzene removal in using a latex membrane (Fitch *et al.*, 2003). Parameters that counteract these side-effects are the degree of cross linking and the molecular weight of the membrane polymer used.

3.3 Membrane Thickness

Micro-porous and dense-phase membranes are made in a variety of different thicknesses, but most membranes have a thickness of around 150-800 μm . The membrane thickness is preferably as small as possible, but needs to have a certain thickness for mechanical stability. When composite membranes are used, the micro-porous membrane is used only for support of the dense-phase layer. In that case, the

dense-phase layer can be kept very thin ($< 10 \mu\text{m}$) and is usually located on only one side of the microporous membrane.

3.4 Membrane and Reactor Configuration

The reactor configuration is dictated by the membrane configuration. Membrane configurations are possible in two basic shapes: tubular or flat. The choice of membrane configuration can be based on optimizing biomass removal, but is most likely based on optimizing mass-transfer. Mass-transfer is a transport phenomenon that is similar to heat transfer in heat exchangers. In general the tubular configuration is most likely the most optimal configuration for a membrane bioreactor because of a higher surface area to volume ratio. However, the cost of the various membrane materials, their shape and their availability currently determines choices of membrane and reactor configurations.

3.5 Airflow Dynamics

Air flow dynamics of a membrane bioreactor are important for optimal treatment as well as energy requirements during operations. The energy requirement is directly related to pressure drop over the bioreactor system. Low pressure drop values should be an important objective when designing a membrane bioreactor for waste gas treatment. Figure 2 shows an example of the pressure drop as a function of the inner diameter of tubular membranes. Larger diameters are associated with lower pressure drop. However, larger diameters also reduce the total surface area of the membrane, which limits the total mass-transfer and the size of the active biofilm.

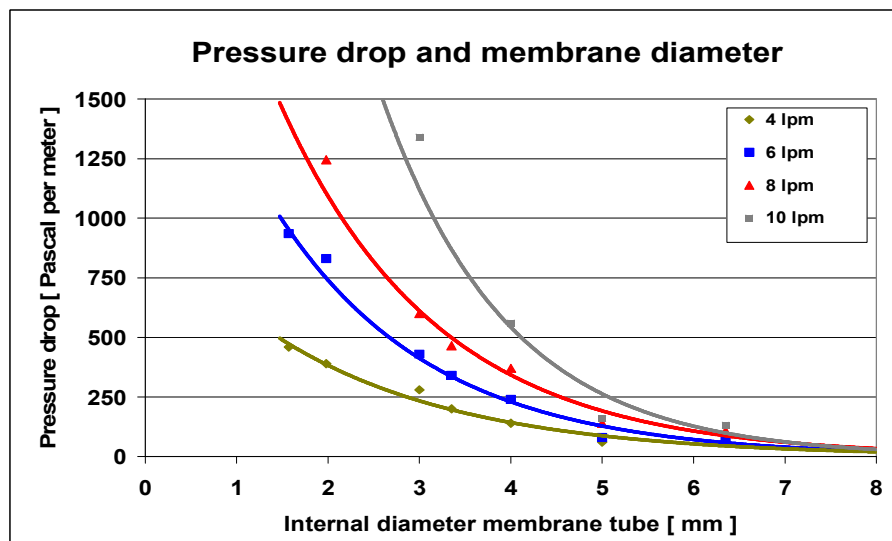


Figure 2: The pressure drop versus internal diameters of a single hollow fiber PDMS membrane at gas flow rates of 4, 6, 8 and 10 liters per minute.

3.6 Water flow

Water with nutrients is usually recirculated, buffered to sustain a neutral pH and refreshed occasionally to add nutrients or remove degradation products. The direction of the water flow can be current or counter-current to the gas flow direction. The water flow recirculation rate is an important parameter in order to maintain minimal differences in pH or nutrients concentration in the membrane bioreactor.

The water flow rate is especially of importance for the control of the amount of biomass in the bioreactor that might accumulate at high inlet pollutant loads. Water flow rate will generate shear forces that can discharge inactive biomass.

3.7 Biomass Control

The membrane separates the gas phase from the biofilm layer on the liquid side, which improves the possibilities to control the biological process. The most active micro-organisms of the biofilm layer are located directly adjacent to the membrane surface, which makes it possible to easily discharge inactive biomass from the reactor. Water flow can generate shear forces on the biofilm layer that erodes only the top layer. An increase of water flow rates will enhance this process called biomass sloughing. The most active zone in the biofilm is likely limited to 0.2 mm or less. Studer showed that a biofilm of less than 1 mm could easily be maintained at relatively low shear forces (Studer, 2005).

An alternative method of removing biomass is the intermittent use of aerators. Large gas bubbles will generate shear forces that removes excess biomass. This has already become common practice over the last years in full-scale membrane bioreactors for industrial and municipal wastewater treatment.

4 APPLICATION FIELDS

An application field of increasing interest for newly developed biological gas treatment technologies is the treatment of waste gases from chemical industries that emit waste gasses with relatively high pollutant concentrations. At what pollutant concentration do conventional biotechniques like biofilters or biotrickling filters starts to have difficulties treating waste gas, especially in relation to control the biomass growth? Biomass accumulation in conventional biofilters and biotrickling filters relates to the total pollutant load per reactor volume (Ozis, 2005). For most pollutants, an average pollutant loading higher than 50 gram of carbon per m³ reactor volume per hour will most likely sooner or later lead to biomass accumulation in a conventional biofilter.

Up to what concentration in the waste gas is the conventional technique incineration not self-supporting and does it require input of fuel for the incineration process? Calculations show that waste gas with a concentration range between approximately 0.4 – 4 g/m³ is interesting for most contaminants for future applications of newly developed biological waste gas treatment systems (Bioway, 2007).

Other specific fields of application are the printing and paint industries, where relatively poorly water-soluble solvents are used. That normally leads to high treatment costs as these compounds are relatively difficult to remove by conventional waste gas treatment techniques. Relatively small facilities often face high capital investments for incinerators that often can not operate under economically feasible circumstances.

Biological treatment is only possible when temperature is in a suitable range for the micro-organisms that are used. As the gas phase is separated from the biomass at the liquid side of the membrane, membrane bioreactors can also be applied for the treatment of relatively hot off-gasses. The recirculating liquid can be used for heat

exchange to keep the biofilm at the required temperature range for optimal biological degradation.

Not only airstreams with relatively high temperatures or high concentrations are suitable for further development of membrane bioreactors. Also airstreams with very low concentrations, such as indoor air, form an interesting application field (Llewellyn and Dixon, 2006) as for example an increase in air humidity (often unwanted in the case of indoor environments) can be avoided using membranes technology. As the air stream is completely separated from the biomass by the membrane, the risk of airborne particles possibly containing unwanted microbes from the biological treatment system is also eliminated. The application of membrane biofilters for air quality control in space crafts (van Ras *et al.*, 2006) as well as a variety of occupied terrestrial environments is currently being investigated. Long term space missions require a sustainable air purification technology that uses a minimum energy demand and does not generate any waste products, which membrane biotechnology can provide.

5 CONCLUSIONS

Bioreactors using membranes are of interest for new applications as they have some important advantages over conventional waste gas treatment systems, including conventional biological waste gas treatment systems. Challenges are still present as an extra resistance for mass transfer from the gas phase to the biofilm might be introduced using a membrane. Thinner and cheaper membranes are required. Research and development have a current focus on the design of the systems that require input of basic parameters like permeability of pollutants for the membrane material and optimal reactor configurations.

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