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**M**embrane supported  
biofilm reactors, a  
literature review

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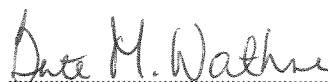
<p>Abstract</p> <p>Membrane supported biofilm reactor is a new technology for biological degradation of pollutants. The utilisation of membranes as a support for biofilm growth may occur in treatment of several types of wastewater, as removing of nitrogen from municipal wastewater or removing of specific pollutants from industrial wastewaters. The advantages of such a technology are a better aeration control process than most other biofilm reactors, and the possibility of bubble-free aeration in the removal of VOC compounds. Moreover, for many kinds of treatment like nitrification/denitrification, the MSBR may give a rather compact solution. At the present the major disadvantages of this technology is the lack of knowledge of the cost of such a membrane and of full scale operation.</p>
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# **Membrane supported biofilm reactors**

a literature review

## **Preface**

This report was written by Francois Catsivilas, ESIGEC, France, and Lars J. Hem, NIVA, while the former was serving as a trainee at NIVA during the summer and autumn 1996.

The quality assurance was done by Bjørnar Nordeide.

Oslo, December 2<sup>nd</sup> 1996.

*Lars J. Hem*

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# 1. Introduction

Various types of carriers for biofilm are used in waste water treatment, and several natural and synthetic materials are applicable. The use of membranes for biofilm support are studied during the last ten years, and this concept has certain advantages.

This litteratur studie was accomplished in order to describe the membrane supported biofilm reactor, and review the experiences with the use of membrane supported biofilm reactors.

## 2. Immobilisation techniques in wastewater treatment

### 2.1 Classification of immobilised cell systems

Karel & al. (1985) divided immobilisation techniques into four categories based on the physical mechanism which causes immobilisation :

- Attachment to a surface.
- Entrapment within a porous matrix.
- Containment behind a barrier.
- Self aggregation.

Examples of the four categories are shown in Figure 1 (Karel & al. 1985).

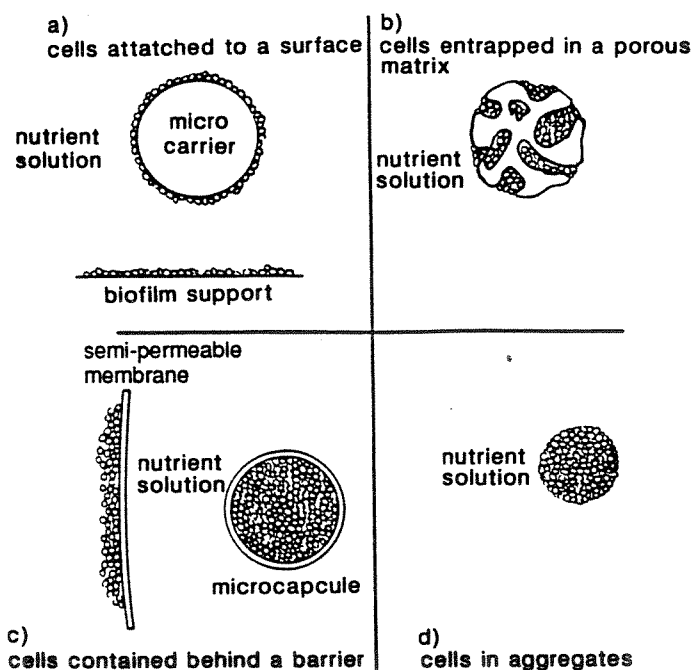


Figure 1. The four categories of immobilisation of whole cells (Karel & al. 1985).

Attachment to a surface is widely used in wastewater treatment as the biofilm process. For nitrification purposes trickling filters, rotating biological contactors and submerged biological filters are the most common attached-biomass processes.

Entrapment within foam cubes has been used for upgrading activated sludge plants (Morper and Wildmoser, 1990, Hegemann and Wildmoser, 1986).

Neither containment behind a barrier nor self aggregation have been reported to have any considerable use in wastewater treatment for nitrification purposes.

## 2.2 Definition of a biofilm

A biofilm is a culture of micro-organisms growing on some surface. the media may be made of nearly any material, but in wastewater treatment processes rock, wood and plastic materials are most common.

The composition of the biofilm will vary depending on the bulk water composition including the oxygen content.

Figure 2 gives a schematic presentation of a biofilm (Harremöes 1978).

As the figure indicates, diffusion will be an important process for the overall efficiency of a biofilm reactor.

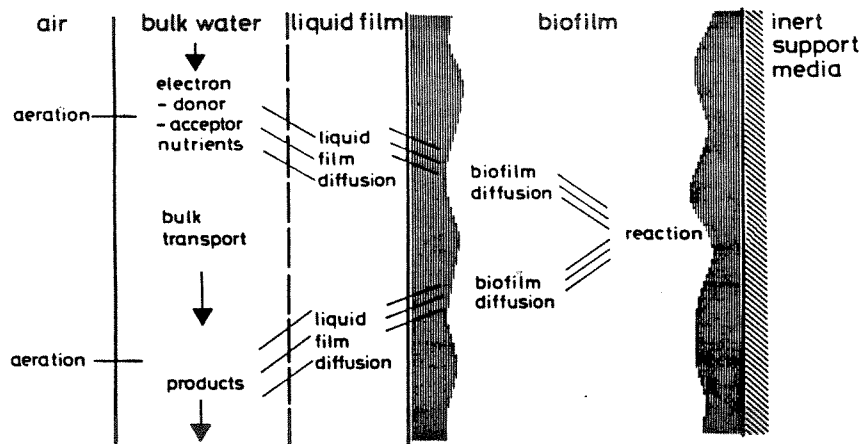


Figure 2. A schematic presentation of a biofilm and the potentially rate-limiting mechanisms



## 2.3 Biofilm kinetics

The growth and development of a biofilm depends on several factors.

Bryers & Characklis (1982) suggested that biofilm development at turbulent flow conditions is the net result of the following biological and transport processes:

- Adsorption of dissolved components at the biofilm surface.
- Transport of suspended particles to the surface.
- Micro-organism adhesion to the surface.
- Metabolic conversions within the biofilm including the growth and decay processes.
- Biofilm detachment.

They also found that biofilm production due to microbial cell reproduction and extracellular polymer production was the major positive contributor to the biofilm accumulation. attachment of suspended biomass was found to be directly proportional to the suspended biomass concentration, but was generally thought to be of minor importance.

The biofilm production will of course be dependant on the composition of the bulk water, and also on the transport processes which decide to what extent dissolved components are available for the micro-organisms in the film.

Rittmann (1989) devided biofilm detachment into four different mechanisms :

- Predator harvesting.
- Shearing caused by water flowing past the solid surface.
- abrasion.
- Sloughing.

Shear-loss is highly affected by the shear stress on the biofilm, and can therefor be reduced by an irregular surface texture which protect the biofilm from shear stress.

Abrasion is most important when the bioparticles are fluidized and is controlled by particles to particles contacts. Both shear-stress and abrasion will influence the physiological properties of the biofilm, like density and growth rate, which in turn affects the detachment rates.

sloughing appears to be a random, massive removal of biofilm because of oxygen and nutrient limitation in the deeper part of the film (Bryers & Characklis 1982).

Transport of dissolved components from the bulk liquid into the biofilm, and transport of reaction product out of the biofilm, is considered to be a question of molecular diffusion in the biofilm and the liquid film outside the biofilm (Harremöes 1982, Cunningham 1989). the combination of reaction and diffusional resistance may result in the lack of substrate in the deeper part of the biofilm (Harremöes 1982, Rittman & McCarty 1981). Diffusional resistance against the transport of oxygen may even inhibit growth of certain bacteria, such as nitrifies, in activated sludge flocs (Neethling 1988).

The diffusional coefficients in a biofilm may differ from those pure water. Williamson & McCarty (1976) found the coefficient for oxygen, ammonia, nitrite and nitrate in a biofilm to be either slightly less than or equal to the corresponding value in pure water.

Some diffusional coefficients in pure water and nitrifying biofilms are listed in Table 1.

Table 1. Diffusional coefficient for some dissolved components.

Component	Condition	Diffusion coefficient in m <sup>2</sup> /s	Reference
Ammonia	Nitrifying biofilm, 20°C	1.50 · 10 <sup>-9</sup>	Williamson and McCarty (1976).
Oxygen		2.5 · 10 <sup>-9</sup>	
Nitrite		1.39 · 10 <sup>-9</sup>	
Nitrate		1.62 · 10 <sup>-9</sup>	
Ammonia	Pure water, 20°C	1.74 · 10 <sup>-9</sup>	Hung and Dinius (1972) cited in Williamson and McCarty (1976).
Oxygen	Pure water, 20°C	3.0 · 10 <sup>-9</sup>	
Oxygen	10°C, pure water	1.44 · 10 <sup>-9</sup>	Landolt-Börnstein (1969) cited in Gujer and Boller (1986) and Harremoes (1978).
	15°C	1.70 · 10 <sup>-9</sup>	
	20°C	2.0 · 10 <sup>-9</sup>	
	25°C	2.4 · 10 <sup>-9</sup>	
Ammonia	10°C	1.32 · 10 <sup>-9</sup>	
	15°C	1.50 · 10 <sup>-9</sup>	
	20°C	1.71 · 10 <sup>-9</sup>	
	25°C	1.94 · 10 <sup>-9</sup>	
Bicarbonate	10°C	8.1 · 10 <sup>-10</sup>	
	15°C	9.3 · 10 <sup>-10</sup>	
	20°C	1.05 · 10 <sup>-9</sup>	
	25°C	1.19 · 10 <sup>-9</sup>	
Carbonds-oxide	10°C	1.22 · 10 <sup>-9</sup>	
	15°C	1.41 · 10 <sup>-9</sup>	
	20°C	1.63 · 10 <sup>-9</sup>	
	25°C	1.90 · 10 <sup>-9</sup>	

The variation and changes in shape or structure of a biofilm are often neglected when the film is modelled or described, and this omission may result in erroneous models (Christensen et al., 1989). Kugaprasatham et al. (1990) found that long-term changes (several days) in turbulent intensity for a nitrifying biofilm under substrate limiting conditions caused changing in the macrostructure of the film. Relatively high turbulent intensity caused a film with fluttering filament, but this disappeared when the turbulent intensity was reduced. The long-term effect of reduced turbulent intensity measured as specific flux (length/time) was more drastic than the short-term effects. The latter could be described by the following diffusion model for fluttering biofilms under turbulent conditions proposed by Nagaroka et al. (1988):

$$D = L \sqrt{u^2}$$

Where :

D = Diffusion coefficient (in biofilm) (length<sup>2</sup>/time)

$\sqrt{u^2}$  = Turbulent intensity near biofilm (Length/time)

L = Dimension of filamentous biofilm (length)

Another example of structure changes, is the changes caused by outbreak of nitrogen bubbles in a denitrifying biofilm (Christensen et al., 1989). These outbreak increase the reaction rate due to changed transport properties of the film

From this it is obvious that the "history" of a biofilm is important when the effects on short-term variations are discussed. Even though the measured mean biofilm thicknesses and the biomass are the same, other properties of the film may differ due to different "histories".

### 3. Biofilm on porous membranes used in wastewater treatment.

#### 3.1 The motivation for developing and using the technology of membrane supported biofilm reactors

The advantage of the membrane supported biofilm reactor (MSBR) compared with the classic biofilm systems is the possibility of separating different phases involved in the degradation of pollutant. The possibility of bubblefree aeration through membranes is an advantage when treating VOC-contaminated waters with aerobic biological reactors, since the danger of stripping of VOCs like dichlorethane is avoided (Freitas dos Santos and Livingston, 1995). The MSBR may also give a possibility for a combined nitrification/denitrification in the biofilm, with the heterotrophic bacteria in the part of the biofilm exposed to the wastewater and the nitrifiers in the bottom of the biofilm which is the part of the film exposed to the oxygen.

#### 3.2 Description of the membrane supported biofilm reactor

##### 3.2.1 Membrane material

A great number of organic materials are known to be gas permeable. Among these are polydimethyl siloxane (silicon rubber) or polyetherimide (PI) (Wilderer, 1995). Gas such as oxygen, carbon dioxide or organic solvents may dissolve in and travel through the material, driven by specific concentration gradients.

Table 2: Permeability of various membrane materials at 25 °C (Wilderer, 1995).

Membrane material	Permeability g mm m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup>
Teflon (PTFE)	0.016
natural rubber	0.092
PVC	0.093
Demethylsilicone (silicone rubber, General Electric)	1.929
Silastic 500-1 (Dow Corning)	2.226

The membrane material used for the construction of a membrane biofilm reactor may be non porous such as silicon rubber. Alternatively, porous materials can be used. Candidates for porous membrane materials are made of hydrophobic fibres such as Teflon or polyetherimide (the latter material can be manufactured so that the pore size changes systematically across the membrane) (Wilderer, 1995).

Using microporous materials, if the membrane is made out of hydrophilic material, the bubbles form on the gas side of the membrane and the pores are filled with water. This situation should be avoided because the diffusion coefficients in water are very small and result in high mass transfer resistance. If the membrane is made of hydrophobic material, the bubbles form on the water side of the membrane and the pores are filled with gas mixture. In this situation the transport mechanism through the pores would depend on membrane morphology, the nature of the gas mixture and the total pressure.

### 3.2.2 Membrane technology

Different kind of technology can be used for the bubble-free aeration. Hollow fibers similar to those used for ultrafiltration can be used for the MSBR. But a new technology using dense silicon rubber tubing seems more efficient. (Wilderer, 1995)

Two different set-ups for reactors with dense silicon rubber tubing membranes are presented in Figure 3. The wastewater to be treated is pumped through the inner part of the tubing (left), or the oxygen is blown through the inner part of the tubing (right).

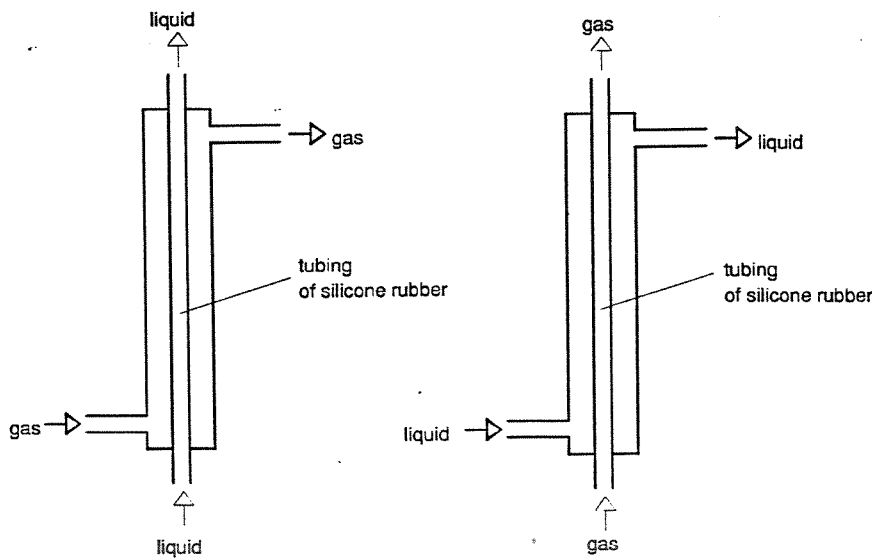


Figure 3: Schematic representation of tubular MSBRs. (Wilderer, 1995).

The solution shown at the left hand side leads to what is called "external mass exchanger". The tubing through which the wastewater is pumped are installed outside the reactor. Water is pumped from the reactor through the inner part of the tubing and back into the reactor. Biofilms grow at the surface of the membrane.

The advantage of external mass exchangers is that the hydrodynamic conditions at the biofilm-liquid interface can be closely controlled. External mass exchangers can be prefabricated. Several modules can be operated in parallel, with the number of modules in service being alternated according to the actual needs.

The "internal mass exchanger" (Figure 3, right) requires the construction of tubing in the reactor. The tubing may be arranged in the reactor in a structure way, or just packed in caches. The latter solution is easy to set up and is thus of significant practical advantages (Wilderer, 1995).

The principle for the construction of a flat membrane sandwich reactor is illustrated in Figure 4. In practice, such a reactor resembles flat membranes ultrafiltration units as those used for gas-gas separation, for instance. Gas and wastewater is passed through the respective chambers of the reactor in zig-zag flow pattern. The gas compartment contain a porous material to keep the membranes from collapsing (spacer) (Wilderer, 1995).

Experiences have already been done on activated carbon membranes Which could reduce the duration of treatment cycles (Kolb and Wilderer, 1995).

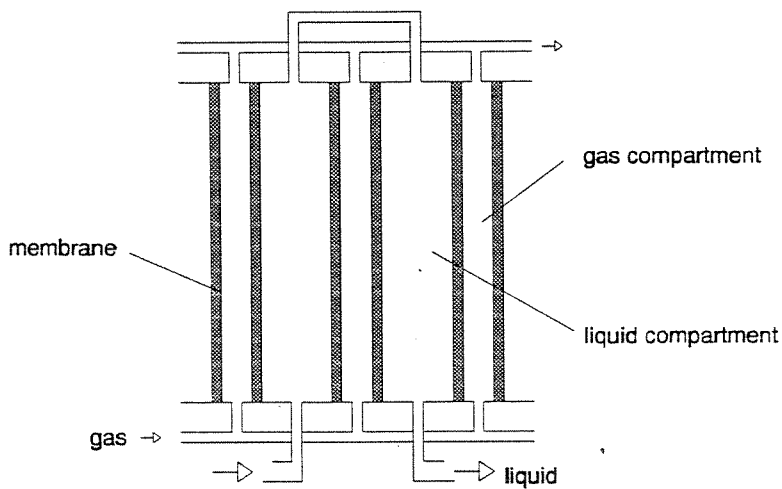


Figure 4: Schematic representation of a flat membrane biofilm reactor (Wilderer, 1995).

Depending on the toxic to be removed, the pollution consistency, or other parameters, biofilm can be either in the wastewater side or in the other side.

For example for a biofilm with combined nitrification and denitrification, the biofilm is located in the wastewater side and oxygen is provided from the other side (fig 5-left)

When DCE contaminated wastewater is to be treated, the biofilm is in the biomedium side and wastewater in the other side. (fig 5-right)

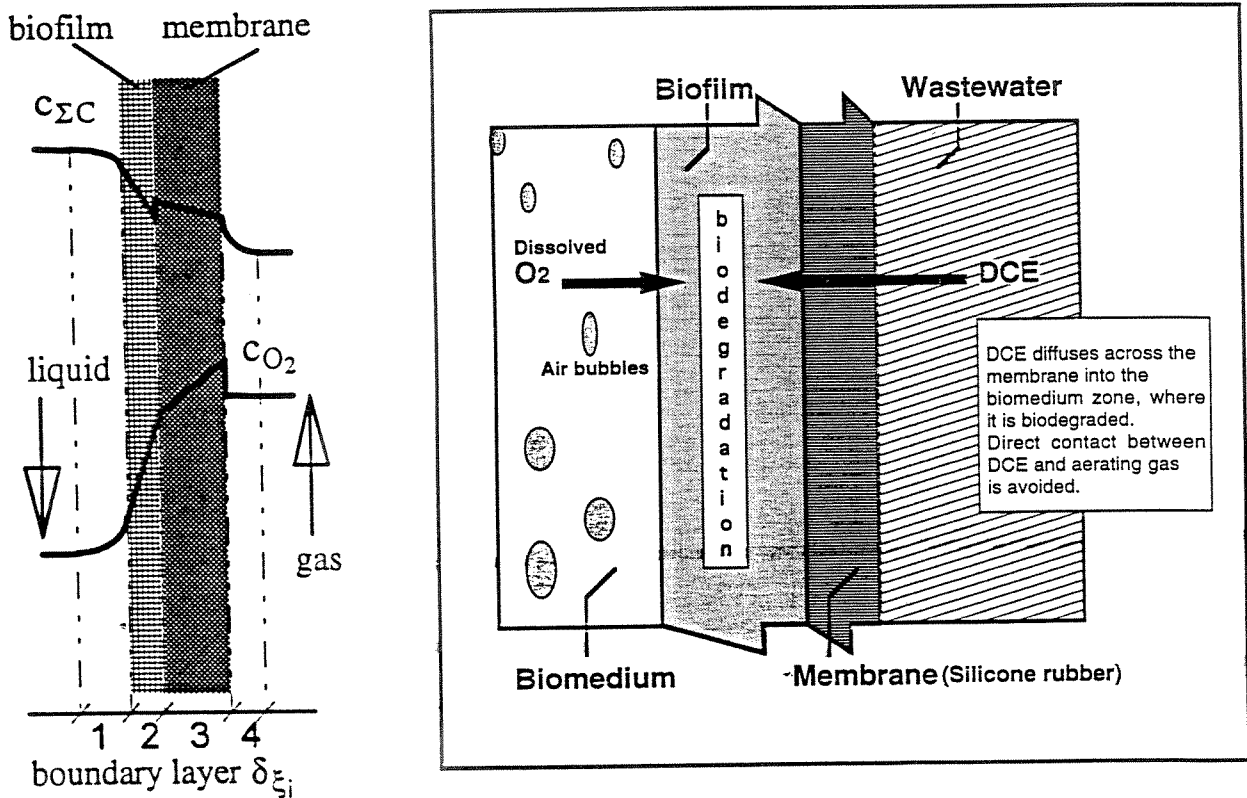


Figure 5: Principle of silicone rubber membrane used to treat DCE contaminated wastewaters (Freitas dos Santos and Livingston, 1995).

### 3.3 Applications for the MSBR

#### 3.3.1 Treatment of domestic wastewater

In the past inadequate oxygen transfer rate with porous materials has made the culture of microbial cells with a high oxygen demand difficult.

With this new type of process, a higher oxygen transfer can be realised without squandering  $O_2$  and energy, and a successful removal of COD at high volumetric loading and short HRT can be realised (Chiemchaisri et al., 1992, Pankhania et al., 1994).

Nitrification and denitrification can be carried out in separate MSBRs (Bock et al., McCleaf and Schroeder, 1995), or in the same MSBR (Chiemchaisri, 1992). The possibility of combined nitrification and denitrification in the same biofilm is unique for this technology.

Using, in a tank filled with wastewater, a gas permeable membrane tubing through which oxygen is supplied, colonization of the membrane occurs as shown in Figure 6.

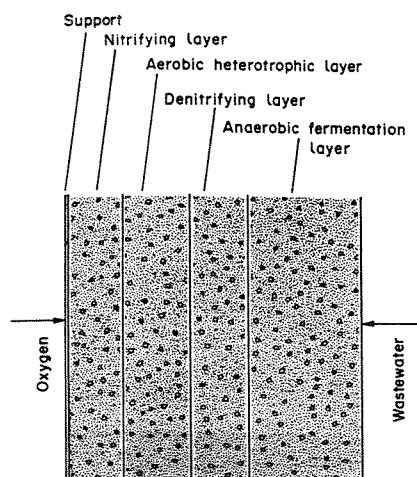


Figure 6: Structure of support aerated biofilm (Timberlake et al., 1988).

Microorganisms near the membrane are provided with oxygen as  $\text{NH}_3$  can diffuse through the biofilm, and nitrification can occur.  $\text{NO}_3^-$  created is concentrated in this first part of the biofilm. Microorganisms based near the biofilm-wastewater interface are in anoxic conditions. So they can easily remove nitrites located near their layer.

### 3.3.2 Removal of VOC compounds

After having dissolved VOC compounds in water by emulsion and phase separation, the degradation of the VOC may be carried out in a MSBR.

For several pollutants (like xylene, DCE, phenols ...etc) the biodegradation can reach to more than 90% (Freitas dos Santos and Livingston, 1995, Kolb and Wilderer, 1995, Debus, 1995, Debus et al., 1994). With this process, the compound produced stays dissolved inside the water avoiding toxic gas escape.

### 3.3.3 Hazardous waste treatments

This MSBR allows the growth of several types of microorganisms (bacteria, fungus...) specialized in the conversion of recalcitrant or hazardous pollutants. By this way, cultivation of fungus like *Phanerochaete chrysosporium* allows the removal of DDT, dioxin, lindane, trinitrotoluene or other polyaromatic hydrocarbons. (Venkatadri and Irvine, 1993).



## **4. Conclusion**

The utilisation of membranes as a support for biofilm growth may occur in several types of wastewater treatment going from typical municipal wastewater to the removing of specific pollutants. The advantages of such a technology are a better aeration control process with a lower residence time and a high contact time (100%), and the possibility of bubble-free aeration in the removal of VOC compounds. Moreover, for many kinds of treatment like nitrification/denitrification, the MSBR may give a rather compact solution.

At the present the major disadvantages of this technology is the lack of knowledge of the cost of such a membrane and of full scale operation.

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