WASTEWATER TREATMENT WITH BIOFILM MEMBRANE REACTORS

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SUMMARY

This paper presents a recent application of microporous hydrophobic membranes: the biomembrane reactors. The objetives of this work are the study of the characteristics of biofilms on permeable suports, as well as how this kind of reactors perform in the removal of carbonaceous organic material and in nitrification and denitrification. Four laboratory bench-scale biomembrane reactors have been used. Two of them were built with flat membranes and the other two with tubular membranes. The reactors have been operated under diferent substrate loading and oxygen availability conditions. The flat membrane reactors gave a loading removal capacity of over 180 $g/m^2/d$ and a performance of 90% with pure oxygen and 75% with pressurized air. The tubular reactors had a lower performance. A nitrogen removal of 47 $gN/m^2/d$ and 11 $gN/m^2/d$ in flat membrane reactors, with air and oxygen respectively, was obtanied. In tubular membrane reactors 4.66 $gN/m^2/d$ were removed. In all reactors a simultaneous nitrification and denitrification was observed. It was possible to operate the reactors without oxygenation cost.

KEYWORDS: Biofilm, membrane, oxygen, permeable support, simultaneous nitrification-denitrification, transfer, diffusion.

INTRODUCTION

There are numerous applications for membranes in fluid/fluid separations in fields such as medecine, biotechnology, hydrometallurgy, and water treatment. The most common applications used in water treatment are microfiltration and ultrafiltration, reverse osmosis, non-dispersive extraction, and liquid membranes. Biological treatments using this kind of membrane as a support for biofilms in wastewater treatment are also available. Together, the membrane and biofilm may be considered as a two-layered membrane: one layer is biologically inert and the other active. The membrane-biofilm unit has been named the ***biomembrane***, and reactors of this type have been called ***biomembrane reactors***.

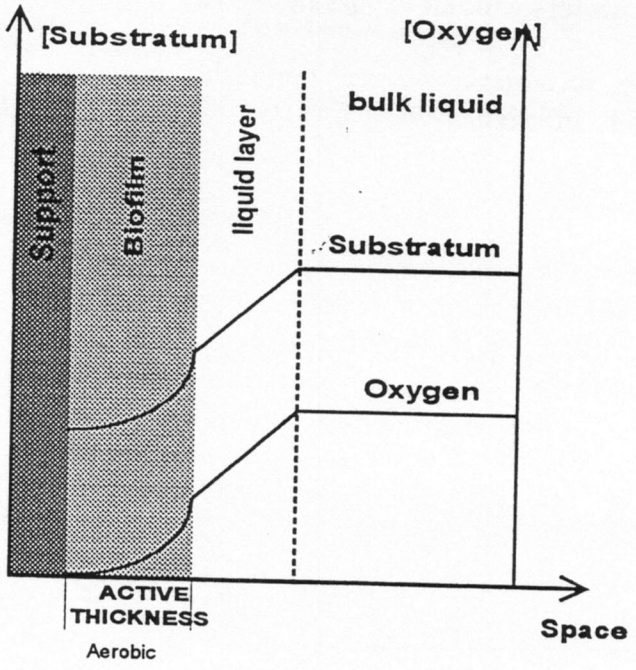
In some of these treatments the membrane fulfills another role as well as that of support. It may act as a filter for substances disolved in the wastewater which, if not first removed, may prove toxic to the biomass on the biofilm and thus impede the biological degradation of the target compound(s). In our case, the membrane acts as a biofilm oxygenation system as it contacts the biofilm with a gaseous space which may contain mixtures ranging from pure oxygen to air. In order to differentiate them from other types of biomembrane reactors, they have been called ***gas permeable support biomembrane reactors***. Various designs of this type of reactor are available in the literature (Abdel-Warith et al. 1990, Eguía 1991, Jácome et al. 1995, Onishi et al. 1982, Osa 1995, Timberlake et al. 1988, Vidart 1992).

BIOFILMS ON GAS PERMEABLE MEMBRANES

In conventional biofilm reactors (trickling filters, RBCs, biofilters, etc.) the biofilm is fixed to an inert or inactive support and the reactants (electron donars and acceptors in the biological reaction) flow in the same direction (*concurrent* flow). For example, in aerobic biofilms the flow of organic carbonaceous material, nutrients and oxygen is in the same direction. From now on in this paper the organic carbonaceous material and the nutrients will be known as the substrate.

On the other hand, in a reactor using a biofilm on a gas permeable support in which the support also provides oxygen to the system, the oxygen flow passes through the support towards the biofilm, while the substrate flows in the opposite direction, from the bulk liquid towards the biofilm (*countercurrent* flow).

In a biofilm reactor the performance of the process is limited by the transfer of reactants into the interior of the biofilm and the evacuation of byproducts from the biofilm. The transfer of substrates to the interior of the biofilm involves three phenomena: advective transfer, molecular diffusion and/or turbulent diffusion. According to the double layer theory, the strongest diffusional resistance takes place in the stagnant liquid layer in contact with, and inside, the biofilm, where transfer is produced exclusively by molecular diffusion. In a well-mixed reactor the concentration of substrates is kept constant throughout the bulk liquid and only drops when it passes through the stagnant liquid layer and the biofilm. If the concentrations of substrate and oxygen are not zero on any part of the biofilm, then both diffuse to the support, this is known as a *totally penetrated biofilm*. If this is not the case, then it is known as a *partially penetrated biofilm*. In this latter type, an active thickness may be defined, which, for example, from the point of view of biological aerobic degradation, would correspond to the thickness of the biofilm through which oxygen and organic material are able to diffuse (Figure 1). Observe how the active layer would be in the most external part of the biofilm and that the highest concentrations of oxygen and substrates correspond in space, as do the lowest concentrations. Generally, the thickness up to which organic material is diffused is greater than that for oxygen, given that the concentration of oxygen in the bulk liquid is much lower, and that the diffusional resistances are the same. For a biofilm to be totally or partially penetrated depends on its thickness.



Figures 1. Oxygen and substrate profiles in a conventional biofilm.

In a biofilm on a gas permeable support the substrate is transferred to the biofilm in the same way as in a conventional biofilm reactor, however, the oxygen is transferred in the opposite direction through the membrane. This difference means that the oxygen and substrate profiles cross. When the biofilm is partially penetrated the active thickness is found in the most internal layer. Also, the place in the biofilm with the

highest oxygen concentrations is found right next to the support, just where the substrate concentration is lowest (Figure 2).

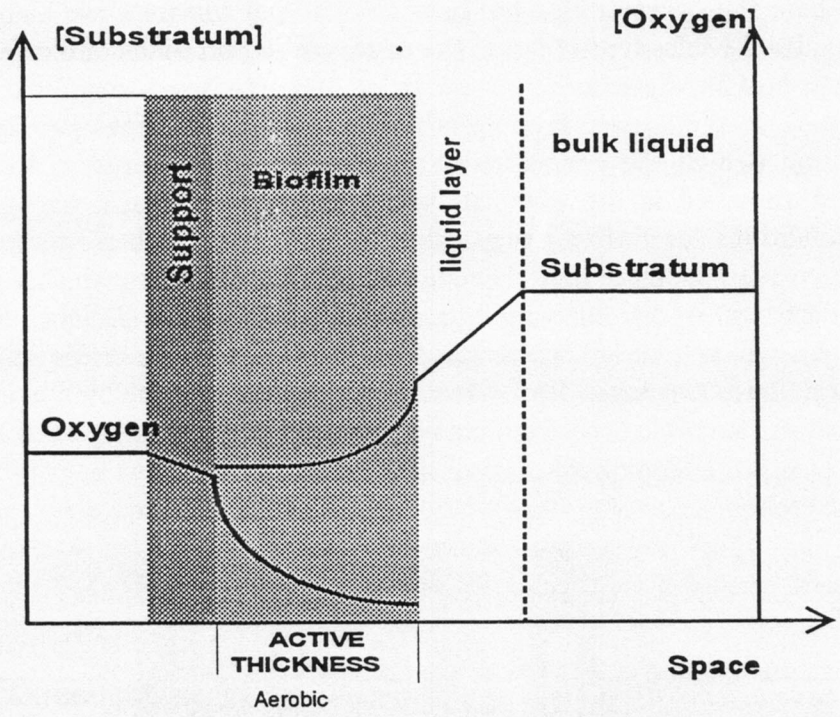


Figure 2. Oxygen and substrate profiles in a biofilm on a permeable support.

The functional differences between types of biological reactors exist because their individual characteristics induce specific environmental conditions which determine the type of predominant organisms and, in turn, the type of reactions which will take place. In a biofilm reactor different environments can also be genereated in the direction of the support depending on the concentrations of substrates on the outside of the biofilm and on the diffusional resistances which will determine the concentration profiles of the reactants. So the availability of oxygen theoretically determines the existance of various layers, each of which has a different environment. In a conventional biofilm reactor, these layers, from the support to the bulk liquid, will be: anaerobic, anoxic and aerobic. While in gas permeable biomembrane reactors the order of the layers reverses, and in the specific case that oxygen were present in the bulk liquid, the order of the layers would be: aerobic, anoxic, anaerobic, anoxic and aerobic. The distribution of substrate may also be defined theoretically by the different layers. Both in conventional reactors and in gas permeable membrane reactors the flow of the substrates is from the bulk liquid, through the biofilm, to the support. Therefore, the greatest availability of substrates will be in the biofilm layer in contact with the bulk liquid, gradually reducing in quantity towards the support.

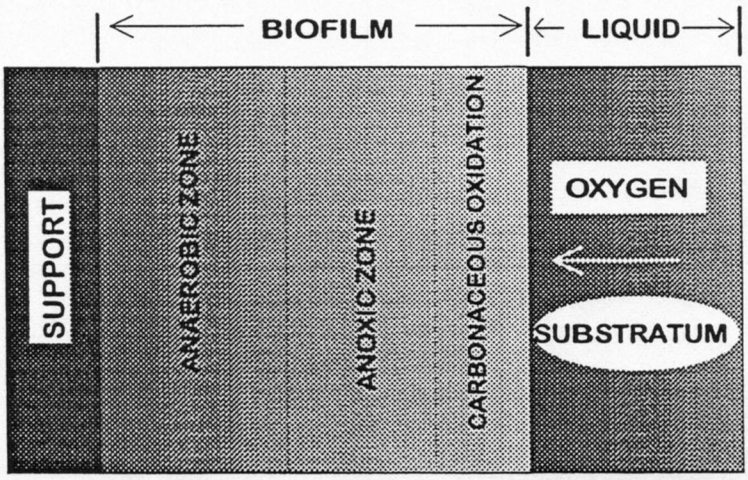


Figure 3. Theoretical zoning of a conventional thick biofilm.

Depending on the different relative concentrations of reactants inside the biofilm, various layers can be distinguished in which different processes take place. In a conventional biofilm reactor in the area closest to the bulk liquid, where the concentrations of both oxygen and substrate are high, the organic carbonaceous material will be oxidised while, depending on the relative concentrations of oxygen and substrate in the more internal layers of the biofilm, the anaerobic degradation, nitrification, or anaerobic digestion of the biofilm will take place (Figure 3). In the deepest layer of a biofilm reactor with a gas permeable membrane, where the oxygen concentration is high, the concentration of organic carbonaceous material may be low (because it may all have been removed in the external layers) and the amoniacal nitrogen may be available, thus producing ideal conditions for nitrifying organisms. In the layers which are furthest from the support where the dissolved oxygen reaches, there may be a high availability of carbon which will be used by heterotrophic organisms to the detriment of the nitrifying organisms. Closer to the bulk liquid, where the dissolved oxygen does not reach, there will be a supply of nitrates from inside the biofilm and a supply of carbon from outside thus producing ideal conditions for denitrification. If the thickness of the biofilm allows it, suitable conditions for the development of anaerobic bacteria could be produced in the more external layers (Figure 4).

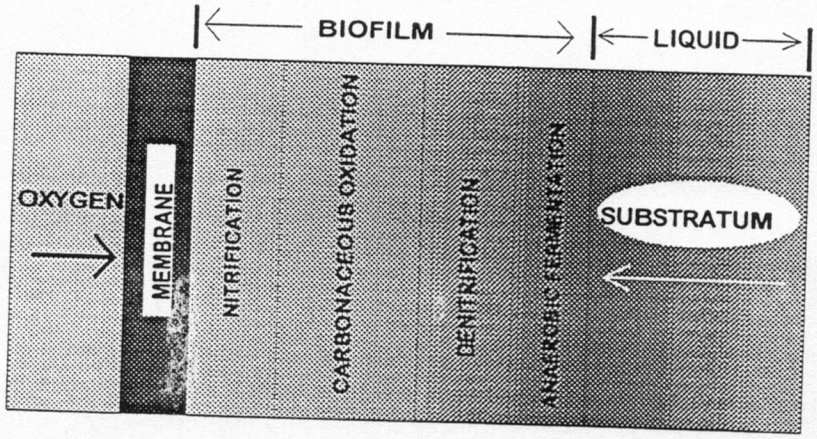


Figure 4. Theoretical zoning of a thick biofilm on a gas permeable membrane.

OXYGENATION CAPACITY

In any aerobic biological process the purification capacity is determined by the oxygenation capacity, therefore, it is vitally important to determine the oxygenation capacity of the system. The results obtained by the non stationary (or sulphite) method, using laboratory scale reactors indicate a low capacity of oxygenation (Table 1). This is because the area of the gas/liquid interface is much lower than in an oxygenation system with bubbles or with surface agitation. It has also been observed that the oxygenation capacity increases with bulk liquid agitation or when the partial oxygen pressure on the gaseous side of the membrane is increased. Bulk liquid agitation reduces the thickness of the stagnant liquid layer and hence reduces the diffusional resistance. Increasing the partial oxygen pressure on the gas increases the concentration of the equilibrium given by Henry's law and thus increases the oxygenation capacity.

Kind of reactor	Oxygen supplies	Available gas flow (L/d)	K_La (d^{-1})	Specific oxygenation capacity ($gO_2/m^2/d$)
Flat membrane	Without membrane	-	0,34	0,08
	Atmospheric air	-	2,92	0,7
	Regulable pressurized air	10	13,16	3,14
		21	24,15	5,86
		43	42,8	10,22
		58	57,1	13,64
Tubular (1)	Atmospheric air	-	6,52	2,17
Tubular (2)	Atmospheric air	-	2,64	6,07
	Pressurized air	-	2,69	6,2
	Pressurized oxygen	-	5,32	12,24

Table 1 Oxygenation capacity of the experimental reactors.

These results are not very promising and seem to indicate that in this kind of reactor much lower than conventional performances will be obtained. But, the determination of the oxygenation capacity using the non steady state method is done without biomass, or in other words, without the biofilm in the reactor and using tap water. The conditions change when the biofilm grows on the membrane. The membrane resists oxygen transfer, but as the biofilm adheres to the support probably there is no stagnant liquid layer. Therefore, as the diffusional resistance of the membrane is lower than that of the stationary liquid layer, the oxygen transfer will be greater.

By performing mass balances with the results obtained from the laboratory scale reactors, using synthetic waste water, and supposing that all the organic material is removed aerobically it can be shown that the oxygen consumed is greater than the oxygenation capacity quantified by the oxygenation test (Table 2). But the hypothesis that no anaerobic degradation is produced is very strong. Therefore, a process has been developed for directly measuring the oxygen consumption of the biofilm. The results of this measurement suggest that the biofilm's oxygen consumption varies with organic load applied, organic load removed, and biofilm thickness. Based on these variables it can be seen that the oxygen consumption may be greater than, the same as, or lower than the oxygenation capacity determined with the non steady state method. Therefore, independently of the air feed, the biofilm consumes only the oxygen it needs. Finally, the anaerobic degradation phenomena become significant in thick biofilms.

Kind of reactor	Kind of supply	K_La (d^{-1})	Specific oxygenation capacity ($gO_2/m^2/d$)	Maximun organic load removed ($gDQO/m^2/d$)
Flat membrane	Pressurized air	57,1	13,64	180
Tubular (1)	Atmospheric air	6,52	2,17	140
Tubular (2)	Atmospheric air	2,64	6,07	17

Table 2. Comparison between oxygenation capacity and organic load removed.

PILOT PLANTS

The Biofilm Group of the University of Cantabria have developed various reactors on a laboratory scale employing different types of membrane and configurations (Figure 5). Two of these employed flat membranes (Eguía 1991, Vidart 1992), the other two used tubular membranes (Jácome et al. 1995, Osa 1995). The characteristics of the pilot plants used in the experimentation are shown in Table 3.

	Eguía (R1)	Vidart (R2)	Jácome (R4)	Osa (R3)
Liquid volume (L)	10,7	1,5	1,6	0,97
Support surface (cm^2)	628,32	628,32	360	36,85
Specific surface (m^2/m^3)	5,872	41,888	22,5	3,799
Kind of membrane	Flat	Flat	Capillary	Capillary
Trade mark	Milipore	Milipore	AKZO	AKZO
Model	PTFE -FGLP	PTFE -FGLP	Accurel ® PP	Accurel ® PP
Material	Politetra-fluoroetylene	Politetra-fluoroetylene	Polypropylene	Polypropylene
Nominal pore size(μm)	0,2	0,2	0,2	0,2
Maximun pore size (μm)			≤ 0,65	≤ 0,65
Mean porosity (%)	70%	70%		
Bubble point, IPA (bar)	≥ 0,91	≥ 0,91	≥ 0,95	≥ 0,95
Mean wall thickness (μm)	175	175	450	1500
Mean inner diameter (μm)	-	-	1800	5500

Table 3. Characteristics of the reactors used.

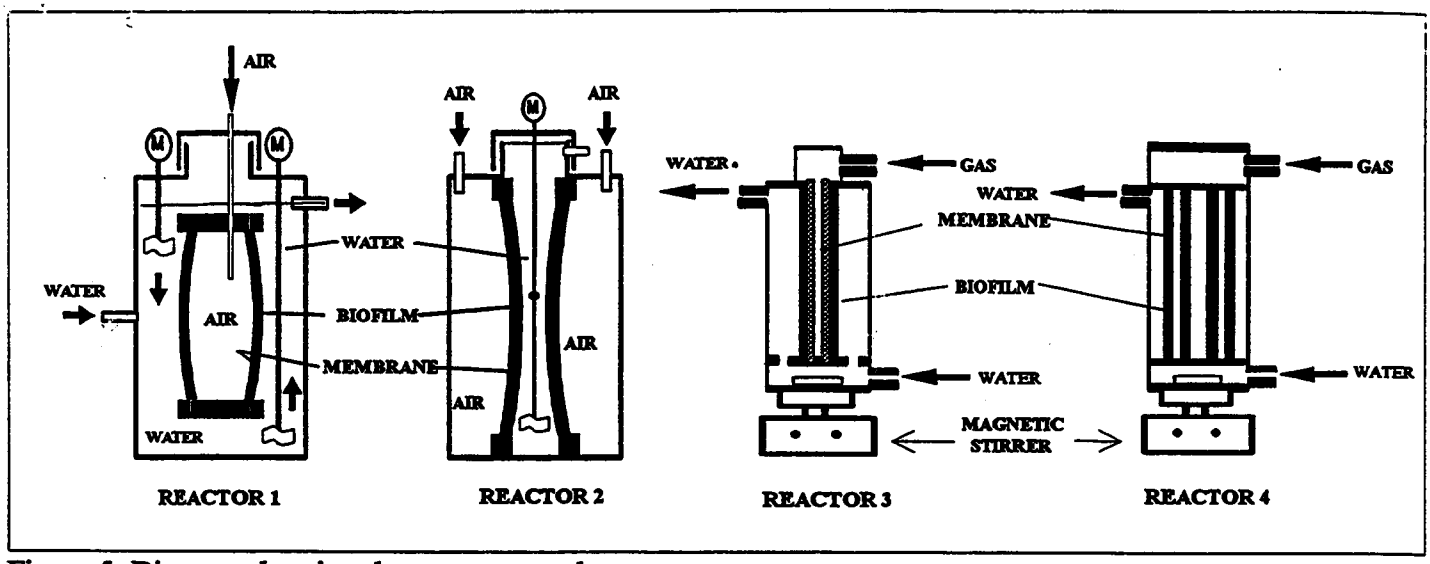


Figure 5. Diagram showing the reactors used.

PERFORMANCE OF GAS PERMEABLE BIOFILM REACTORS

CARBON REMOVAL

The treatment capacity of these systems varies with the type of membrane, reactor configuration, etc. Flat membrane reactors obtain removals of up to 180 g COD/m^2/d. This value is one order of magnitude greater than the values used in the design of RBCs. The organic load removed, generaly follows Monod or Blackman type kinetics with respect to the organic load applied (OLA). Therefore, greater removals are not obtained with applied organic loads greater than the saturation value, which lies between 150 and 200 g COD/m^2/d. The saturation value or maximum removable load is influenced by the availability of O_2 (Figure 6). These reactors can work with OLAs greater than the saturation value. OLAs up to 600 g COD/m^2/d have been used without detecting any performance anomalies.

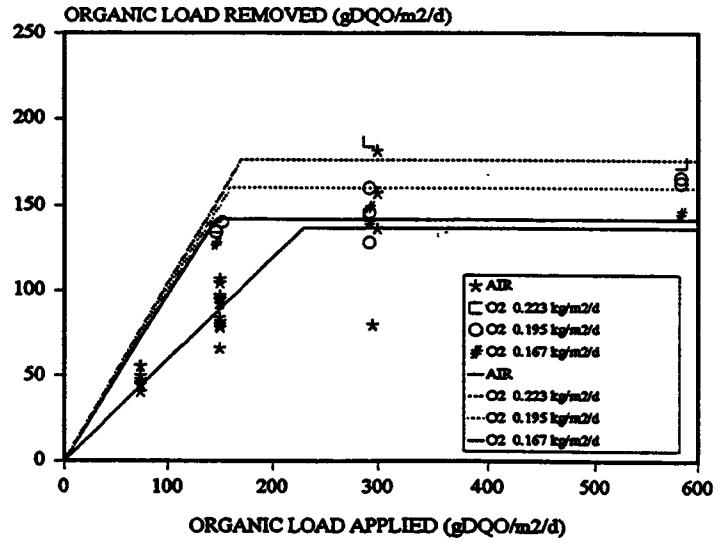


Figure 6. Organic load removed vs. organic load applied, in a flat membrane reactor using air. Influence of oxygen availability.

When pure oxygen is used as the feed gas and the OLA is less than or equal to the maximum removable load, then performances of up to 90% or more can be achieved. If air is used as the reactor feed gas then high levels of purification can be obtained, but the performance does not improve on 75%.

When the treatment capacity is analysed with respect to the biofilm's thickness, in all cases it is possible to detect a reduction in the capacity to remove carbon when the thickness of the biofilm is increased (Fig. 7). This is due to the increase of the diffusional length of the substrate caused when the biofilm thickness increases, and the thickness of the active layer decreases.

Removal capacities of up to 192 g COD/m^2/d have been obtained using hollow fibre reactors. But, although the kinetics are the same as for flat membrane reactors, the performances obtained are rarely greater than 80%, and normally are always under 50%. This is probably because the membrane is much thicker in this type of reactor and the diffusional limitations are therefore greater, thus reducing oxygen availability.

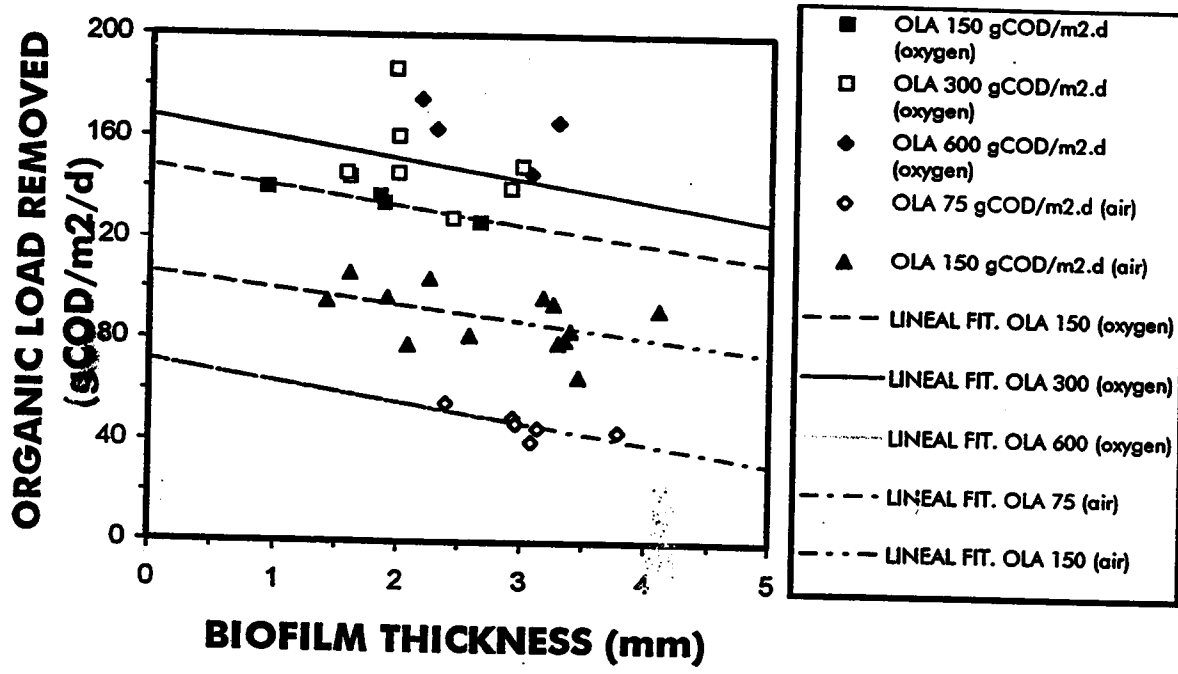


Figure 7. Influence of biofilm thickness on treatment capacity (organic load removed). Biofilm on membrane using air and oxygen.

NITROGEN REMOVAL

Flat membrane reactors using synthetic wastewater at concentrations equivalent to municipal wastewater have been found to have negligible levels of nitrates and nitrites in the effluent. The nitrogen removal capacity, using air as the feed gas, has reached extraordinary values of up to 47 g N/m^2/d (Figure 8). Such high values are due to the fact that in this type of reactor nitrification and denitrification occur simultaneously. When pure oxygen is used as the feed gas the maximum nitrogen load removed is not greater than 11 g N/m^2/d. This is explained by the inhibition of the nitrifying organisms caused by the high oxygen concentrations found in the layer in contact with the membrane.

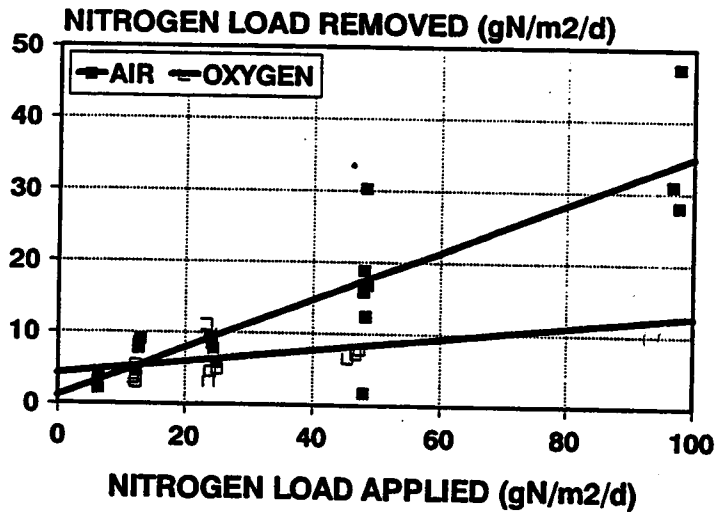


Figure 8. Comparison of the performance of a biofilm on membrane, with respect to nitrogen removal, using oxygen and air.

The maximum rate of nitrification obtained using capillary membrane reactors is 4.66 g $N/m^2/d$. Both in flat membrane and capillary membrane reactors, the removal of carbonaceous organic material, nitrification and denitrification take place simultaneously in the same biofilm. This is because the oxygen and substrate profiles generate different environments, causing the stratification of the heterotrophic, nitrifying and denitrifying organisms in the biofilm.

In flat membrane reactors, using air, the carbon/nitrogen ratio in the influent water has an irregular influence on nitrogen removal (Figure 9). In this case, the carbon/nitrogen ratio in the influent does determine the proportion in which carbon and nitrogen are removed from the system (Figure 10). It has also been observed that the capacity for denitrification depends on the concentration of nitrates. Therefore, when the reactor is fed with increasing quantities of nitrogen in the form of nitrates (up to 60 mg/l N_NO_3), the concentration of nitrites in the effluent increases, reaching concentrations of up to 23 mg/l N_NO_2 (9).

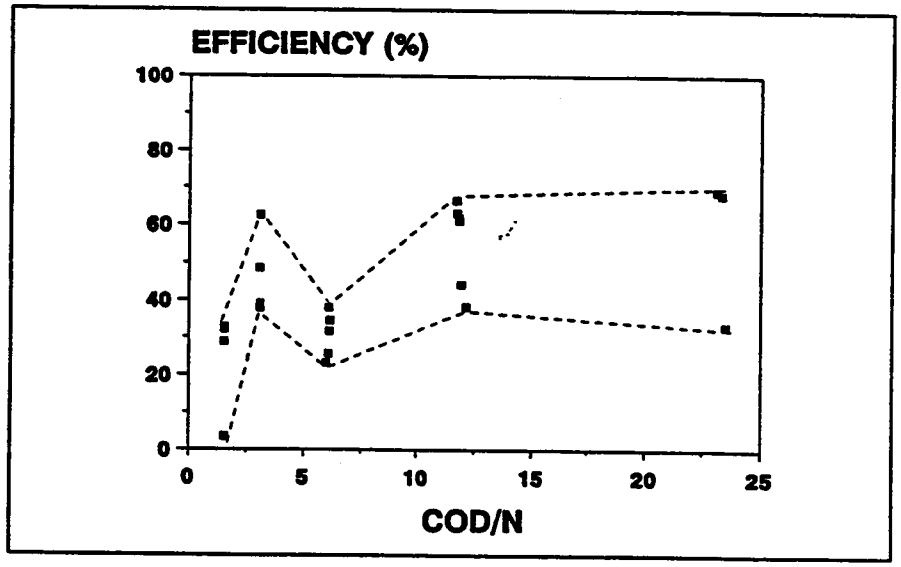


Figure 9. Influence of feed COD/N ratio on the performance of nitrogen removal for a membrane biofilm using air.

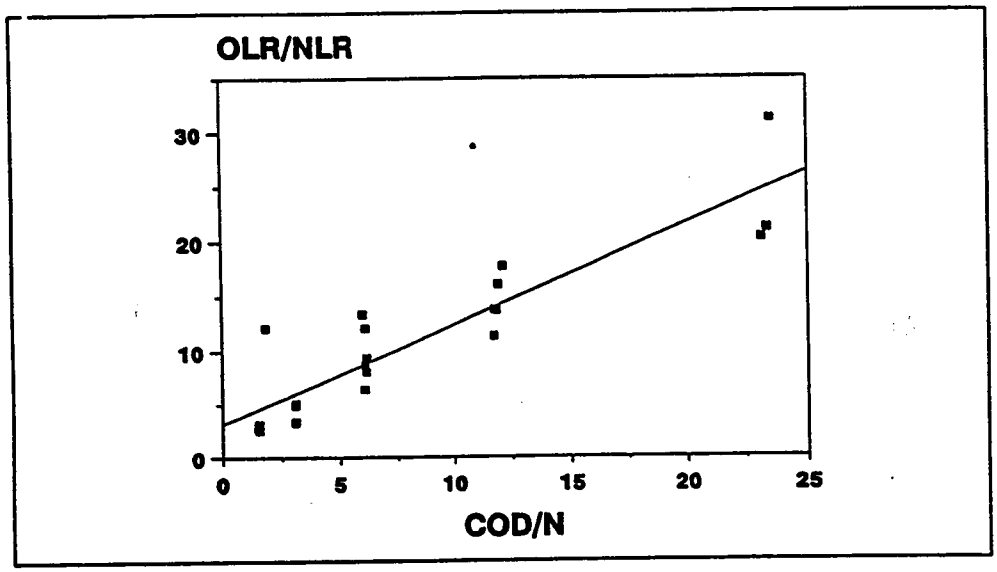


Figure 10. Effect of feed COD/N ratio on the proportion of organic load/nitrogen load removed for a membrane biofilm using air.

BIOFILM CHARACTERISTICS

The membranes developed on gas permeable supports have been thick and dense. Under experimental load conditions, the concentration of solids in the biofilm (density) has been maintained within a range of 80 to 105 Kg/m^3, equalling the maximum values for very thin (100 μm) conventional biofilms, while in our case these concentrations were given for measured thicknesses of between 1 and 4 mm. For these thickness values, conventional biofilms normally present solids concentrations of between 20 and 30 kg/m^3 (Fig. 11). This difference may be explained by the way in which the biofilm grows. While in a conventional reactor the biofilm grows on the surface, which is where the aerobic heterotrophic bacteria are, the biofilm grows from within in reactors using gas permeable supports. It has also been observed that the age of a biofilm influences its thickness (Fig. 12).

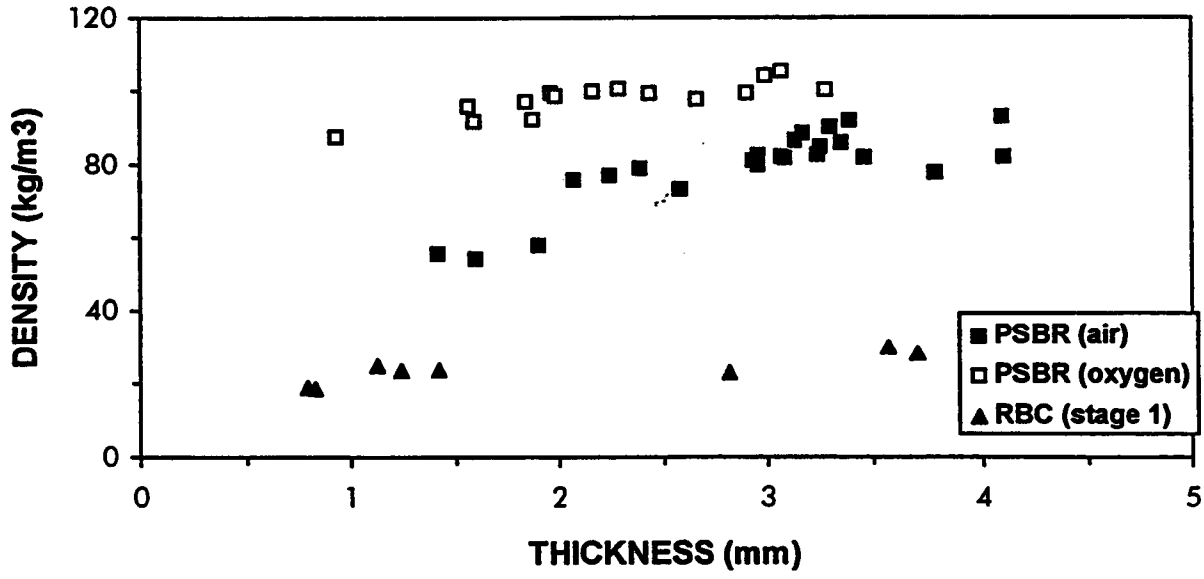


Figure 11: Solids concentrations with respect to thickness, in a biomembrane using air and oxygen.

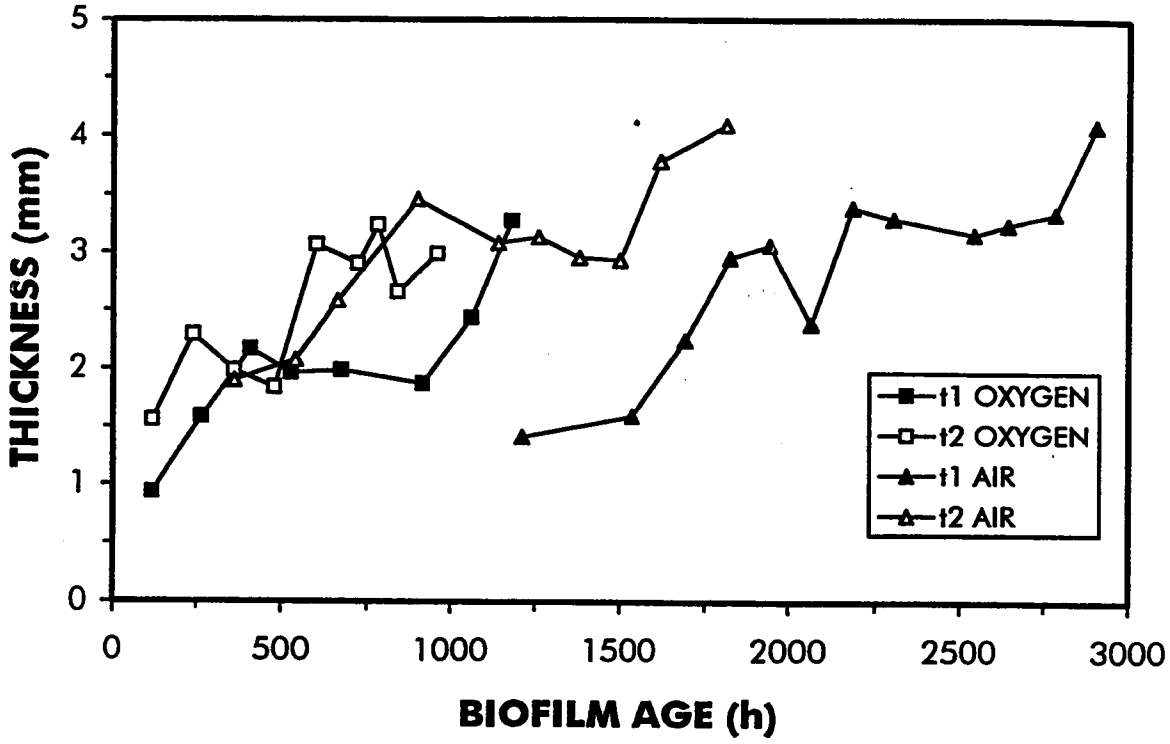


Figure 12. Influence of biofilm age on thickness for biomembrane using oxygen or air and an RBC in the 1st. stage.

PRODUCTION OF SLUDGE AND SUSPENDED SOLIDS IN EFFLUENT

The concentration of suspended solids (SS) in the effluent, without clarifying, was found to be low (5 to 33 mg SS/l), suggesting that in some cases it may be possible to do without secondary clarifying. The low effluent contamination by SS is due to the low production of sludge by the system (0.10 to 0.30 g SS/g BOD removed), explained by the aerobic and anaerobic digestion of the biomass inside the biofilm.

SUMMARY AND CONCLUSIONS

The following observations can be made about biomembrane reactors on gas permeable supports:

- As thickness is increased, the purifying capacity is reduced due to the increase in the diffusional resistance of the biofilm.
- The system's oxygenation capacity is much greater with biofilm than without owing to the phenomena of biological oxygen transfer.
- It is not necessary to artificially supply oxygen to the biofilm through the membrane, as the biofilm takes it directly from the air through the membrane.
- They have a high solids concentration (density), which is comparable with high thicknesses, due to the way they grow from inside the biofilm.
- They have a very low sloughing rate (low sludge production) owing to the simultaneous aerobic-anaerobic digestion of the biofilm matrix.
- They have a high capacity for carbon and nitrogen removal (nitrification-denitrification), which take place simultaneously, permitting the treatment of clarified wastewaters.

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