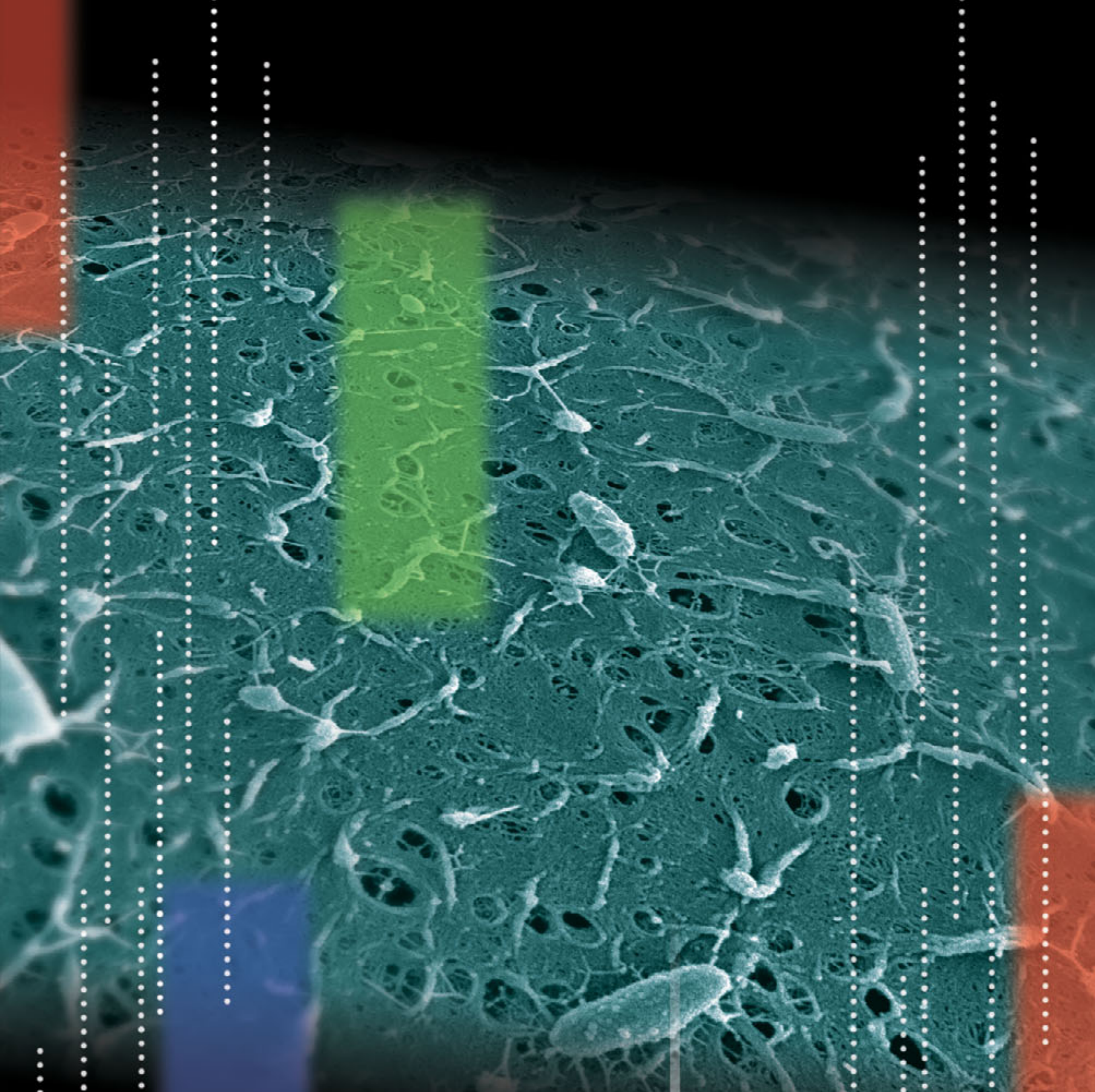

Anaerobic membrane bioreactors for wastewater treatment

Feasibility and potential applications

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2006

ANAEROBIC MEMBRANE BIOREACTORS FOR WASTEWATER TREATMENT:

FEASIBILITY AND POTENTIAL APPLICATIONS

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ABSTRACT

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Biomass retention is a necessary feature for the successful application of anaerobic digestion for wastewater treatment. Biofilms and granule formation are the traditional way to achieve such retention, enabling reactor operation at high biomass concentrations, and therefore at high organic loading rates. Membrane filtration represents an alternative way to achieve biomass retention. In membrane bioreactors, complete biomass retention can be achieved, irrespective of cells capacity to form biofilms or granules. Membrane bioreactor systems represent then a promising technology for those conditions where biomass aggregation cannot be ensured, or when an effluent completely free of suspended solids is of interest.

In the present thesis the feasibility of anaerobic membrane bioreactors (AnMBR) is described, under a wide range of conditions and reactor configurations, which are listed in Table A.1. Applied biomass concentrations during AnMBRs operation were in the range 20-45 g/L.

Table A.1: Continuous operation of AnMBRs during the present thesis.

Temperature	Configuration	Membrane	Substrate
Thermophilic	Submerged	Polymeric	VFA
Thermophilic	Submerged	Polymeric	Glucose, VFA
Mesophilic	Submerged	Polymeric	VFA
Mesophilic	Submerged	Polymeric	VFA, potato peels
Thermophilic	Submerged	Polymeric	VFA, potato peels
Thermophilic	Side-stream	Ceramic	VFA
Thermophilic	Side-stream	Ceramic	Ethanol, starch, gelatine
Mesophilic	Side-stream*	Polymeric	VFA in presence of high salinity

* Operated with gas sparging inside the membrane tube (with no forced liquid circulation)

Under all conditions tested, cake formation showed to be the limiting factor determining the applicable flux. Low levels of irreversible fouling were observed, irrespective of the reactor configuration, temperature, type of substrate or membrane material. The latter is of great importance for the long term operation of the AnMBRs. Due to its effect over back-transport mechanisms, particle size showed to be a determining factor for the applicable fluxes. Under thermophilic conditions, the development of a fraction of small particles, most likely originated from cells decay, produced an important influence on the filtration performance. Consequently, physiological effects of temperature on the properties and composition of the sludge are much more important for membrane filtration than the physical effect of temperature on sludge or permeate rheology. The presence of non-acidified organic matter in the wastewater showed to significantly affect the physical properties of the sludge by inducing the growth of suspended acidogenic biomass, which negatively affected the applicable fluxes.

Under the conditions of this study, no indication was found regarding a possible negative effect of the shear stress generated by the cross-flow liquid velocity on the substrate conversion rate, via microbial syntrophic consortia. However, exposure of the sludge to a high shear stress affected sludge properties, reducing the attainable flux, most likely due to a reduction in particle size.

Results show that the application of anaerobic membrane bioreactors is an efficient way to retain specific bacteria that can be key for the treatment of wastewaters under extreme conditions. The latter would enable their application to a wide range of industrial processes with the purpose of water recycling. The challenge for future research is finding the optimum operational conditions to control the cake layer formation, enhancing membrane performance and reducing the membrane area requirements. This will increase the economic feasibility of AnMBRs, enabling its full scale application.

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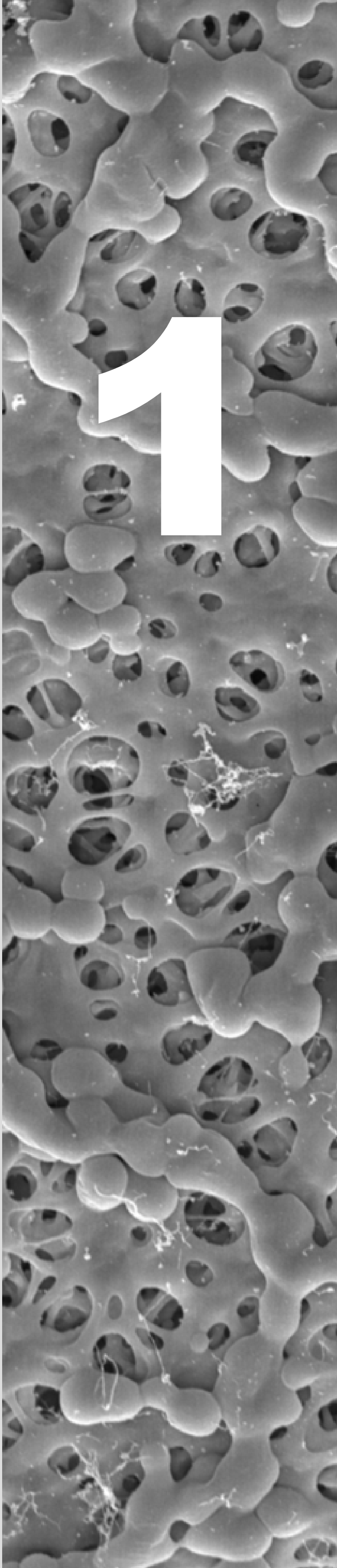
Application of biomass retention by membrane filtration to anaerobic digestion



1.1. ENVIRONMENTAL BIOTECHNOLOGY AND BIOMASS RETENTION

Biological waste treatment processes play a central role in the way societies manage their wastewaters. It is based on the activity of a wide range of microorganisms, converting the organic pollutants present in the wastewater. The treatment capacity is directly related to the amount of microorganisms that can be effectively retained in the treatment system. The role of biological sludge in wastewater purification was firstly identified by Arden and Lockett (1914), almost a century ago. Since then, different ways to enhance biomass retention have been implemented. The traditional way to achieve a high biomass concentration in wastewater treatment systems is by post-reactor sludge settling, followed by recirculation of the settled sludge to the biological reactor. This is still the most common way to manage biological solids in aerobic wastewater treatment systems, even though gravity clarifiers are widely recognised as the weakest link in activated sludge systems. Biomass retention can also be accomplished by biofilm formation, which greatly facilitates biomass-liquid separation. Biofilms are very useful in environmental biotechnology since they ensure an effective uncoupling of sludge retention time from liquid retention time, enabling the treatment of large volumes of diluted aqueous solutions, at short liquid retention times (Nicolella *et al.*, 2000).

Low biomass yields and low growth rates represent one of the important advantages of anaerobic biotechnology, since they translate into the generation of low amounts of waste sludge, up to ten times less than during aerobic treatment. However, during the first developments of anaerobic processes this feature represented a major drawback when trying to increase the biomass concentration in anaerobic reactors (Speece, 1996). The development of biofilm based reactors represents an important milestone in the development of anaerobic reactor technology for wastewater treatment, enabling reactor operation at elevated biomass concentrations. The anaerobic filter was the first anaerobic reactor which considered solid-liquid separation (Young and McCarty, 1967). However, it was the recognition of the anaerobic sludge granulation concept what most significantly contributed to the development and application of anaerobic high rate treatment process. Since the installation of the first full scale upflow anaerobic sludge blanket (UASB) reactor, three decades ago (Lettinga *et al.*, 1980), anaerobic process has been successfully used for the treatment of many kinds of industrial wastewaters as well as sewage. Nowadays, it can be considered an established technology, that offers the possibility of an efficient treatment with low capital and operational costs (Lettinga *et al.*, 1997). From the available anaerobic technologies, sludge bed reactors are by far the most applied. Different types of granular sludge based reactors are nowadays available. The UASB reactor, the expanded granular sludge bed (EGSB) reactor, and the internal circulation (IC) reactor are the most common examples. At present close to 80% of all full-scale anaerobic installations are sludge bed reactors in which biomass retention is attained by the formation of sludge granules. Obviously, the granulation process represents a key factor in the operation of these high-rate anaerobic reactors. Several conditions have been identified to play an important role in the formation and stability of anaerobic granules. Both, wastewater characteristics and operational conditions have been shown to be of determinative importance (Schmidt and Ahring, 1996; Batstone and Keller, 2001; Liu *et al.*, 2002; Liu *et al.*, 2003; Hulshoff Pol *et al.*, 2004). From the cited studies it can be concluded that granule formation is a complex process involving physical-chemical as well as biological interactions.

The increase in industrial processes efficiency has lead to more effective utilization of raw materials and supplies. The same applies to the use of water, which leads to the generation of wastewaters with more extreme characteristics, such as elevated temperatures and high contents of organic pollutants and salts. Consequently, an increasing need of processes capable of achieving an efficient treatment under extreme operational conditions can be expected for the future. This is especially true when recycling of wastewater as process water is considered. However, under extreme conditions, anaerobic biomass immobilization through biofilms or granule formation may result difficult.

Immobilization of thermophilic microorganisms for instance, seems to be more problematic than mesophilic microorganisms. High temperatures reduce the production of extracellular polymers (Schmidt and Ahring, 1994; Quarmby and Forster, 1995), a key factor for biomass aggregation. Less strong granules (Quarmby and Forster, 1995), no granulation (Uemura and Harada, 1993) or even de-granulation when mesophilic granules are used as inoculum (van Lier *et al.*, 1992; Fang and Lau, 1996) have been reported. When working with anaerobic filters with high saline wastewater, Mendez *et al.* (1995) observed a notorious lower performance under thermophilic conditions in comparison with mesophilic conditions, due to low biomass retention.

Effluent turbidity seems to be a common problem during the treatment of saline wastewaters. Cell plasmolysis, lack of filamentous microorganisms and absence of protozoa have been issued as reasons for high turbidity during the treatment of hypersaline wastewaters under aerobic conditions (Woolard and Irvine, 1995; Lefebvre and Moletta, 2006). High wastewater density also contributes to the problem by reducing the settling velocity of dispersed particles. In anaerobic biofilm formation, high salinity may have a positive role on the early stages of biomass aggregation, due to the presence of cations that condense the electrical double layer, resulting in a stronger effect of the attractive van der Waals forces (DLVO theory). However, the abundant presence of monovalent cations likely disturbs the cross linking between bio-polymers, and thus bacterial aggregation, generally attained by bivalent cations like Ca^{2+}. Sowers and Gunsalus (1988) observed that adaptation of *Methanosarcina thermophila* to high NaCl concentrations is accompanied by a reduction in the production of the heteropolysaccharide outer layer, and its growth as single cells or in small aggregates. However, Schmidt and Ahring (1993b) disputed this finding, suggesting that the reason for single cell growth was more related with the selected substrate than with the high NaCl concentration. They observed growth on single cells or small aggregates at Mg^{2+} concentrations higher than 100 mM. Lefebvre *et al.* (2006) observed sludge de-granulation when treating saline tannery soak liquor in a UASB reactor.

The application of granular sludge bed reactors for the treatment of wastewaters with a high content of suspended solids has also limitations. Particulate material can affect the sludge bed development in different ways, like blocking liquid distribution systems, diluting the granular sludge bed with inactive material and favouring growth on the particle surface rather than in granular biomass (Lettinga and Hulshoff Pol, 1991).

In those situations where biofilm or granule formation is severely affected, membrane assisted physical separations can be used to achieve the essential sludge retention. Membrane bioreactors (MBR) ensure biomass retention by the application of micro or ultra filtration processes. This allows operation at high sludge concentrations (Stephenson *et al.*, 2000). Since biomass is physically retained inside the reactor, there is no risk of cells washout and the conversion capacity is apparently non-dependent on the formation of biofilms or granules. In addition, membrane bioreactors offer the possibility to retain specific microorganisms that, in the generally applied upflow reactors, would wash out (Brindle and Stephenson, 1996; Ben Aim and Semmens, 2002; Vallero, 2003). The latter is the case during the anaerobic treatment of specific long chain fatty acids, like oleate. Hwu *et al.* (1998) showed that immobilization of oleate degrading microorganisms is not successfully accomplished under EGSB reactor conditions. Also Kleerebezem *et al.* (1999) found that the microorganisms responsible for the decarboxylation of therephthalic acid to benzoic acid could not be retained in UASB reactors. A clear example of membranes enhanced biomass retention is the high nitrification rates obtained in aerobic MBRs, in comparison with traditional activated sludge, due to a successful retention of slow growing nitrification microorganisms (Shim *et al.*, 2002). MBR systems also appear suitable for the treatment of wastewaters with high content of organic suspended solids, since particles are confined inside the reactor, allowing their degradation (Harada *et al.*, 1994; Fakhru'l-Razi and Noor, 1999; Fuchs *et al.*, 2003). Furthermore, since the permeate is free of solids or cells, water would eventually require less post-treatment steps if reuse or recycle is of interest, in comparison with sludge bed technologies.

So far, the main drawback of MBR systems is related with membrane costs, energy requirements and membrane fouling (vanDijk and Roncken, 1997; Choo *et al.*, 2000; Stowa, 2002). However, important advances have been made in the development of new types of membranes, of which the costs have been significantly reduced (Judd, 2006). In addition, research is being conducted in order to find reactor configurations and operational procedures that reduce fouling and energy consumption.

1.2. MEMBRANE BIOREACTORS FOR WASTEWATER TREATMENT

According to how the membrane is integrated with the bioreactor, two MBR process configurations can be identified: side-stream and submerged (Figure 1.1). In side-stream MBRs membrane modules are placed outside the reactor, and the reactor mixed liquor circulates over a recirculation loop that contains the membrane. In submerged MBRs, the membranes are placed inside the reactor, submerged in the mixed liquor. Side-stream MBRs involve much higher energy requirements, due to higher operational trans-membrane pressures (TMP) and the elevated volumetric flow required to achieve the desired cross-flow velocity. Indeed, pumping requirements for side-stream aerobic MBRs account for 60 to 80 % of the total energy consumption, aeration being only 20 to 40% (Gander *et al.*, 2000). However, side-stream reactors have the advantage that the cleaning operation of membrane modules can be performed more easily in comparison with submerged technology, since membrane extraction from the reactor is needed in the later case. Submerged MBRs involve lower energy needs, but they operate at lower permeate fluxes, since they provide lower levels of membrane surface shear. The latter means higher membrane surface requirements. The selection between submerged and side-stream configurations for aerobic MBRs seems somehow settled, in favour of submerged MBRs. In fact, nowadays, most of the commercial applications are based on the submerged configuration, due to lower associated energy requirements (Judd, 2006).

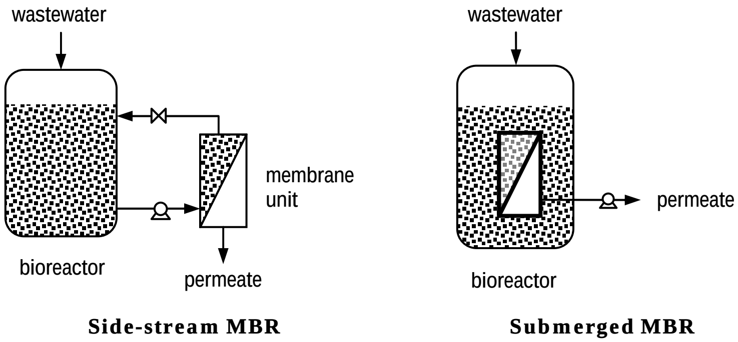


Figure 1.1. Membrane bioreactors for wastewater treatment, according to membrane position.

Most of the reported research done with anaerobic membrane bioreactors (AnMBR) has been performed with the side-stream configuration (Liao *et al.*, 2006). However, the potential negative effect of the circulation of digester broth through the membrane unit, pumps and valves has raised some concern. Anaerobic degradation of organic matter involves the participation of different microorganisms, with complex metabolic interactions. For instance, because of unfavourable thermodynamics, oxidation of propionic and butyric acids is only possible when low hydrogen concentrations are provided, brought about by the electron scavenging action of hydrogenotrophic methanogens. Biofilm formation reduces the transfer distances for hydrogen and other intermediary compounds between the different microorganisms, enhancing syntrophic interactions (Stams, 1994; de Bok *et al.*, 2004). Prove of this is the reduction of the propionate and butyrate degradation rates produced by destruction of granules (Schmidt and Ahring, 1993a; Stams, 1994). During the operation of side-stream AnMBRs, Brockmann and Seyfried (1997), Ghyoot and Verstraete (1997), and Choo and Lee (1996b) observed a decrease in performance that was interpreted as the negative effect of high shear conditions over microbial activity and/or physical interruption of the syntrophic association. However, other authors did not report apparent problems with metabolic activity (Pillay *et al.*, 1994; Fakhru'l-Razi and Noor, 1999; Ince *et al.*, 2001; Fuchs *et al.*, 2003; Padmasiri *et al.*, 2007). This apparent discrepancy about shear conditions over activity may be attributed to operational conditions such as the use of different types of pumps, which can provide different levels of shear, as observed by Kim *et al.* (2001) for aerobic MBRs. Moreover, typical scale down phenomena may add shear-related operational problems. E.g. the frequency of liquid recirculation through the pump is higher for smaller reactors, which means that the effect of pump shear is expected to depend on the reactor scale.

1.3. Membrane fouling and flux reduction in AnMBRs

Membrane fouling is definitively the main drawback of the application of MBRs for wastewater treatment (Flemming *et al.*, 1997). Membranes themselves represent a relevant capital cost, so everything that can reduce their lifetime or the applied flux will directly affect the economic feasibility of the process. Moreover, membrane cleaning activities directly affect reactor operation due to the need for process interruptions. The flux reduction phenomenon is usually analysed in terms of filtration resistances. The flux through the membrane is a function of the TMP, the permeate viscosity (η) and the total resistance (R_T) (Judd, 2006):

$$J = \frac{TMP}{\eta \cdot R_T}$$

in which J represents the applied flux. The total resistance can be divided in several partial resistances (Howell and Nystrom, 1993; Mulder, 1996):

$$R_T = R_M + R_C + R_F + R_{CP}$$

where R_M is the membrane resistance, R_C is the resistance due to cake layer formation over the membrane, R_F is the resistance due to membrane fouling linked to pore blocking and adsorption and R_{CP} is the resistance originated from the formation of the condensation polarization layer. The contribution of the partial resistances to the total resistance is schematically presented in Figure 1.2. Having information about the total resistance distribution in all its partial components is of great benefit. Strategies for flux decline mitigation can only be effective if the causes of flux reduction can be determined.

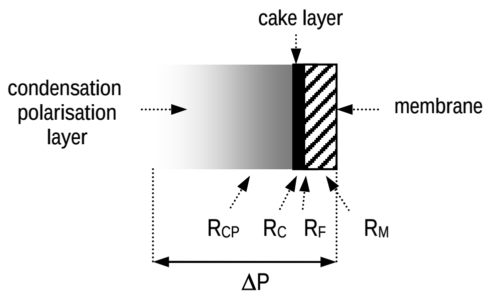


Figure 1.2: Partial filtration resistances during membrane filtration.

Three categories of factors affecting applicable flux can be identified: membrane material and pore size, suspension properties, and operational conditions.

1.3.1. Membrane material and pore size

When selecting the type of membrane to be used in an AnMBR, two main decisions have to be made: materials and pore size. Mainly polymeric membranes have been used in MBR systems for wastewater treatment, based on their lower costs. Membrane hydrophobicity has shown in some studies to play a significant role (Chang and Lee, 1998; Chang *et al.*, 1999; Choo *et al.*, 2000; Stephenson *et al.*, 2000). Hydrophobic protein residues can form strong attachments to hydrophobic membranes resulting in strong fouling (Howell and Nystrom, 1993; Russotti *et al.*, 2001). Indeed, surface modification of hydrophobic polymeric membranes by grafting more hydrophilic polymers can reduce fouling and improve flux (Choo *et al.*, 2000; Russotti *et al.*, 2001; Sainbayar *et al.*, 2001). Membrane material may also determine the applicable fluxes. Kang *et al.* (2002) compared the filtration characteristics of organic and inorganic membranes, observing that flux was determined by internal fouling in inorganic membranes, and the formation of a cake layer over the organic membrane. Ghyoot and Verstraete (1997) also achieved higher fluxes using a ceramic microfiltration membrane, in comparison with a polymeric ultrafiltration membrane. However, these differences in membrane performances may also be the result of structural differences between the membranes, like surface roughness. (Bérubé *et al.*, 2006).

Membrane pore sizes used in wastewater treatment applications are in the range of 0.02-0.5 μm (Stephenson *et al.*, 2000). Several authors have observed the existence of an optimum membrane pore size (Choo and Lee, 1996a; Elmaleh and Abdelmoumni, 1997). This suggest that higher pore sizes may foul more rapidly as a result of blocking by macro-colloids or cells, while those smaller are expected to foul more readily as a result of clogging by micro-colloids, that can adsorb to the internal surface of the pores (Bérubé *et al.*, 2006). It should also be considered that membrane rejection properties are not only defined by membrane pore size but also by the formation of a gel or cake layer, which acts as a secondary dynamic membrane. This phenomena has been observed in both anaerobic and aerobic MBRs (Harada *et al.*, 1994; Pillay *et al.*, 1994; Choi *et al.*, 2005). When long term operation is considered, the formation of cake or gel layers may also reduce the influence of membrane properties over filtration performance, since the membrane is not anymore in direct contact with the suspension.

1.3.2. Suspension properties

Suspension properties can also affect the filtration performance of the membrane. Increasing the suspended solids concentration usually produces a decrease in the attainable flux (Strohwald and Ross, 1992; Pillay *et al.*, 1994; Beaubien *et al.*, 1996). Indeed, convective flow of particles towards the membrane surface is directly related with the suspended solids concentration. Particle size distribution can also strongly determine solids deposition over the membrane surface. The magnitude of back-transport mechanisms, such as shear induced diffusion and inertial lift, are strongly related with particle size (Belfort *et al.*, 1994; Tardieu *et al.*, 1998). For the latter reason smaller particles experience a higher tendency to deposit over the membrane surface than larger particles (Altmann and Ripperger, 1997; Kwon and Vigneswaran, 1998). Sethi and Wiesner (1997) modelled the transient permeate flux in cross-flow microfiltration, predicting an unfavourable size at around 0.4 μm where net back-transport due to Brownian diffusion, shear-induced diffusion and inertial lift is at a minimum, resulting in the highest particle accumulation on the membrane surface. On the other hand, research conducted with model bidispersed and polydispersed suspensions has shown that the smallest particles in the suspension can determine the filtration rate (Kim *et al.*, 2002; Kromkamp *et al.*, 2002; Kromkamp *et al.*, 2006). This means that in complex systems like AnMBRs, filtration flux may be determined by a fraction of the total sludge. Not only suspended solids, such as biomass, can affect membrane permeability, but also many other agents like colloids (Choo *et al.*, 2000), soluble organic matter (Harada *et al.*, 1994), inorganic precipitates (Choo and Lee, 1996b; Yoon *et al.*, 1999) and extracellular polymers (Nagaoka *et al.*, 1996; Chang and Lee, 1998; Cho and Fane, 2002). The relative contribution of all these fouling agents to the overall performance is, of course, determined by the conditions of each particular application.

The modification of suspension properties has been tested in order to enhance membrane filtration. Park et al. (1999) experimented with the addition of powdered activated carbon (PAC) to anaerobic suspended sludge in an AnMBR, with the purpose of adsorbing colloids and soluble compounds. A positive effect was observed at higher cross-flow velocities, most likely due to the scouring effect of the PAC over the membrane surface. Also the use of flocculants has been tested in aerobic MBRs, with positive results (Nguyen and Ripperger, 2002; Yoon et al., 2005). To the knowledge of the author, no reports are available about flocculants application in AnMBRs. The full scale feasibility of either PAC, flocculants or other additives will naturally depend on the compromise between the extent of their effect and the required dosage and frequency of use.

1.3.3. Operational conditions

Operational conditions are the third key factor determining flux reduction. Membrane fouling is usually prevented applying shear over the membrane surface. As already mentioned, in side-stream MBRs this is accomplished by applying high cross-flow velocities. An increase in the cross-flow velocity usually results in an increase of the applicable flux (Beaubien *et al.*, 1996; Elmaleh and Abdelmoumni, 1997; Wisniewski *et al.*, 2000). However high cross-flow velocities can induce a decrease in particle size distribution, increasing the chances for particle deposition (Choo and Lee, 1998). Gas sparging is the most common way to provide high shear conditions in submerged MBRs. Air sparging is widely used in aerobic MBRs, where it carries out a double function: provide oxygen transfer to the liquid phase, and promote scouring of the membrane surface (Cui *et al.*, 2003). In AnMBRs biogas can be recirculated in order to achieve a similar effect. However, very few studies dealing with gas sparged submerged AnMBRs are available. Kayawake *et al.* (1991) reported the beneficial effect of biogas sparging on a submerged membrane during the anaerobic digestion of a heat-treated sewage sludge. Hu and Stuckey (2006) studied the application of a submerged AnMBRs for the treatment of a diluted wastewater. The same group has also done research in the characterisation of soluble microbial products in AnMBRs (Aquino *et al.*, 2006). The application of a gas slug flow regime inside tubular membranes is receiving an increasing attention as a way to control membrane fouling (Cui *et al.*, 2003). At increasing gas flow rates bubbles tend to collide and coalesce, which leads to large bubbles referred to as gas slugs or Taylor bubbles. Bubbles motion generates secondary liquid flows that enhance the liquid-membrane surface mass transfer, especially in the liquid falling film region and the bubble wake (Ghosh and Cui, 1999; Taha and Cui, 2002). Imasaka *et al.* (1989) studied the application of gas slug flow in ceramic membranes, using nitrogen gas. He observed increasing permeate fluxes, at higher gas flow rates.

Several operational procedures have been reported in order to reduce membrane fouling in MBRs: flux stoppage and permeate back-flush are the most common strategies for both aerobic and anaerobic MBRs (Choo and Lee, 1996b; Nagaoka *et al.*, 1996; Park *et al.*, 1997; Ramirez and Davis, 1998; Ognier *et al.*, 2002b; Ognier *et al.*, 2002a; Smith *et al.*, 2006). Unfortunately, they reduce the hydraulic capacity of the reactor, especially back-flushing.

1.4. CRITICAL AND SUSTAINABLE FLUXES

The critical flux concept was introduced over 10 year ago, and has proven useful to characterize membrane fouling in membrane applications, especially in MBRs (Bacchin *et al.*, 2006). The critical flux was originally defined as the flux below which no fouling occurs (Field *et al.*, 1995; Howell, 1995). So, the critical flux is the value at which TMP starts to deviate from the pure water behaviour. The latter is the now called strong definition of the critical flux. However, in complex systems fouling is inevitable, even at no flux conditions. For example, solutes adsorption or crystallization of salts can reduce membrane permeability independently of the applied flux. Consequently the weak definition of the critical flux is usually of more interest, under which the critical flux is defined as the flux over which the relation between flux and TMP becomes non-linear (Wu *et al.*, 1999).

Different methods have been used to determine the critical flux, such as direct membrane observation (Li *et al.*, 1998), mass balances (Kwon *et al.*, 2000) and TMP observation in flux step or cycling experiments (Chen *et al.*, 1997; Wu *et al.*, 1999; Le Clech *et al.*, 2003). Mass balances and microscopic observations are unlikely to be used in full-scale installations or in submerged MBRs. However, pressure increase at constant flux operation can be easily applied for critical flux determination in any type of membrane process, both at lab and full scale.

In MBRs for wastewater treatment, fouling is not avoidable, and indeed the absolute absence of fouling is not at all a necessary condition for the long term operation of MBRs. Then the weak definition of critical flux is usually used when applying membrane processes to wastewater treatment, determined most of the times by TMP evolution during flux step experiments. During this determination a certain threshold criterion has to be established, below which fouling is considered inexistent or acceptable. This criterion will naturally depend on the type of application, and will most likely be determined by the filtration duration and economic considerations. In this respect, MBRs for wastewater treatment constitute a very special application of membrane filtration. They involve continuous operation and membranes are exposed to a complex medium, while systems are not always closely monitored or controlled. Under these conditions, the concept of sustainable flux gains importance, in order to refer to a certain flux which enables long term operation, under low, moderate or tolerable levels of fouling (Bacchin et al., 2006). The definition of this sustainable flux will of course vary depending on the specific application, and how the compromise between a high flux and therefore low membrane requirements is balanced with the occurrence of membrane fouling and maintenance needs.

1.5. ANMBRS FOR WASTEWATER TREATMENT: SPECTRUM OF APPLICATION

Market available high-rate sludge bed reactor systems, such as UASB, EGSB or IC reactors, represent a reliable and low cost treatment alternative for a wide range of wastes, and are nowadays successfully applied under a broad variety of conditions. MBR technology involves much higher costs than high rate granular sludge bed reactors, due to membrane requirements, higher energy demands and higher complexity. Furthermore, capital and operational costs of MBR systems are normally directly related with the applied surface membrane area. Since membrane area requirement linearly increases with the size of the treatment installation, for a given application, the generally experienced economy of scale of most treatment systems is only partially applicable to MBR technology. Under conditions where granular technology can be successfully applied, potential benefits of the application of membrane based processes may be marginal, questionable or even absent if compared with the increases in treatment costs. Complete solids retention is not always needed and residual effluent solids can be removed by more economical and simple means, of course, as long as biomass washout is small and does not put reactor operation at risk. In addition, many applications require an aerobic post-treatment, so anaerobic treatment is not likely to be the final treatment step. A free solids effluent is in most cases not required at an intermediate treatment step, unless an AnMBR is followed by a polishing step like ultrafiltration and reverse osmosis for complete wastewater treatment.

Application of AnMBRs is most likely restricted to conditions or applications where granular sludge technology may or will experience problems. This likely is the case when extreme conditions prevail, such as high temperatures and high salinity, since, as already mentioned, biofilm and granule formation can be severely affected. Following the current trend of increasing water use efficiency and closing industrial process water cycles, these extreme conditions are likely to become more common in the future.

Tables 1.1 and 1.2 present several literature reports about the application of AnMBRs for the treatment of wastes. Table 1.1 presents information regarding the biological performance of the MBRs, while Table 1.2 presents the membrane performances attained during the same researches. Only reports containing continuous operation of AnMBRs have been considered, leaving out reports including only short term filtration tests. These reports show that the application of AnMBRs has been studied so far for a wide variety of wastewaters: sewage, food processing wastewaters, industrial wastewaters, high solids wastewaters. However, the application of membrane filtration to anaerobic digestion processes is still in its developing stage. This is evidenced by an almost complete lack of full scale applications (Liao *et al.*, 2006). Moreover, many researches have applied only low or moderate biomass concentrations, achieving low volumetric organic loading rates.

In their review Liao et al. (2006) refer to the potential applications of AnMBRs. According to them, minimal opportunities for AnMBR application exists for the treatment of high-strength soluble wastewaters, since granular technologies already provide a reliable treatment of these wastes. On the contrary, high-strength particulate wastewaters offer extensive opportunities for the application of AnMBRs, due to its complete solids retention. The authors also consider the application of membrane technology to low strength wastewaters as a future opportunity. However, it must be realised that during the treatment of dilute wastewaters, hydraulic retention time will be low, requiring a high permeate flow, and thus a high permeate flux or a high membrane area.

Table 1.1: Biological performance of AnMBRs for wastewater treatment

Wastewater	**Volume** *(m^3)*	**Temperature** *(°C)*	**MLSS** *(g TSS/L)*	**OLR** *(g COD/L·d)*	**Removal** *(%)*	**References**
Acetate	0.01	35	0.13	-	95	(Elmaleh and Abdelmoumni, 1997; Elmaleh and Abdelmoumni, 1998)
Acetate	0.009	35	5-20	0.8-0.9[a]	95	(Beaubien *et al.*, 1996)
Acetate, ethanol, sulphate (sulphate reduction)	0.006	33	Up to 1.8	-	-	(Vallero *et al.*, 2005)
Starch	0.007	35	16-37[b]	8-24	94-87	(Cadi *et al.*, 1994)
Meat extract and peptone	0.003	35	2.6	1.8	96	(Aquino *et al.*, 2006)
Skim milk and cellulose	0.01	35	Up to 15[b]	1.5-2.5	98	(Harada *et al.*, 1994)
Synthetic	0.0045	54-56	-	-	-	(Choo *et al.*, 2000)
Synthetic	0.009	30	Up to 6[c]	8.3	98-99	(Bailey *et al.*, 1994)
Sweets factory	0.09	35-37	-	8-9	97-99	(Defour *et al.*, 1994)
Maize processing	2610	35	21	3	97	(Ross *et al.*, 1992)

Table 1.1: Biological performance of AnMBRs for wastewater treatment (continued)

Wastewater	**Volume** *(m^3)*	**Temperature** *(°C)*	**MLSS** *(g TSS/L)*	**OLR** *(g COD/L·d)*	**Removal** *(%)*	**References**
Acetic acid Sauerkraut brine Slaughterhouse	0.007	30	20-25 40-60 20-28	20 8 4	90 >95 >95	(Fuchs *et al.*, 2003)
Food industry	0.4	37	6-8	4.5	81-94	(He *et al.*, 2005)
Soybean processing	2	30	-	2.5	71	(Yushina and Hasegawa, 1994)
Brewery	0.12	36	Up to 50^b	Up to 28.5	97-99	(Ince *et al.*, 2000; Ince *et al.*, 2001)
Brewery	0.12	35	31-38	12-20	96-99	(Fakhru'l-Razi, 1994)
Brewery	0.05	35	30	15	97	(Strohwald and Ross, 1992)
Potato starch bleaching	4	-	100-15	1.5-5	65-85	(Brockmann and Seyfried, 1996; Brockmann and Seyfried, 1997)
Palm oil mill	0.05	35	50-57	14.2-21.7	91.7-94.2	(Fakhru'l-Razi and Noor, 1999)
Alcohol distillery	0.004	53-55	0.5	1.5-2	97	(Choo and Lee, 1996b)

Table 1.1: Biological performance of AnMBRs for wastewater treatment (continued)

Wastewater	Volume (m^3)	Temperature (°C)	MLSS (g TSS/L)	OLR (g COD/L·d)	Removal (%)	References
Alcohol fermentation	0.005	55	2	3-3.5	90-95	(Kang *et al.*, 2002)
Molasses	0.005	20	0.16[d]	13	-	(Hernandez *et al.*, 2002)
Wheat starch and gluten production waste	24	37	18	33	-	(Yanagi *et al.*, 1994)
Kraft bleach wastewater	0.015	35	7.6-15.7	-	61[e]	(Hall *et al.*, 1995)
Kraft pulp mill	5	53	8	9-28[f]	86-89	(Imasaka *et al.*, 1993)
Kraft pulp mill	5	53	9	10.7[g]	-	(Minami *et al.*, 1991; Minami, 1994)
Sewage	0.018	24-25	16-22	0.4-11	60-95	(Wen *et al.*, 1999)
Primary sludge	0.12	35	-	0.4-0.68[h]	25-57[i]	(Ghyoot and Verstraete, 1997)
Primary sludge	0.5	35 55	29	0.93-1.94[h] 1.16-2.04[h]	56-49[i] 63-53[i]	(Murata *et al.*, 1994)

Table 1.1: Biological performance of AnMBRs for wastewater treatment (continued)

Wastewater	Volume (m^3)	Temperature (°C)	MLSS (g TSS/L)	OLR (g COD/L·d)	Removal (%)	References
Heat treated sewage sludge	0.2	35-38	10-20	4-16	79-83	(Kayawake *et al.*, 1991)
Macerated pig manure	5	50	4-8%	-	-	(du Preez *et al.*, 2005)
Swine manure	0.006	37	20-40	1-3	-	(Padmasiri *et al.*, 2007)
Cow manure	0.34	55		1.9[h]	49[i]	(Zitomer *et al.*, 2005)

MLSS stands for mixed liquor suspended solids
[a] Load expressed as g COD/gVSS·d
[b] Concentration expressed as g VSS/L
[c] Concentration in the membrane circulation loop
[d] Concentration in contact with filter
[e] AOX removal
[f] Load expressed as g BOD/L·d
[g] Load expressed as g TOC/L·d
[h] Load expressed as g VS/L·d
[i] VS destruction

Table 1.2: Membrane performance of AnMBRs for wastewater treatment

Wastewater	Configuration	Pore size or MWCO	TMP (bar)	Cross-flow velocity (m/s)	Final or mean flux (L/m²·h)	References
Acetate	side-stream	0.14 µm	0.5	3.5	120	(Elmaleh and Abdelmoumni, 1997; Elmaleh and Abdelmoumni, 1998)
Acetate	side-stream	0.2 µm	0.35	2	25	(Beaubien *et al.*, 1996)
Acetate, ethanol, sulphate (sulphate reduction)	Submerged	0.2 µm	0.1-0.4	-	17	(Vallero *et al.*, 2005)
Starch	side-stream	0.2 µm	0.4-0.8	2-2.5	4-14	(Cadi *et al.*, 1994)
Meat extract and peptone	submerged	0.4 µm	0.15 0.25		10 20	(Aquino *et al.*, 2006)
Skim milk and cellulose	side-stream	3000 kDa	0.49	0.8	20-40	(Harada *et al.*, 1994)
Synthetic	side-stream	0.14 µm	0.6-2	0.5-3	-	(Choo *et al.*, 2000)
Synthetic	UASB + side-stream module	-	2-2.5	2.2-3.6	15-20	(Bailey *et al.*, 1994)
Sweets factory	side-stream	60 kDa	5	1	9	(Defour *et al.*, 1994)
Maize processing	side-stream	20–80 kDa	4.5	1.6	37-81	(Ross *et al.*, 1992)

Table 1.2: Membrane performance of AnMBRs for wastewater treatment (continued)

Wastewater	Configuration	Pore size or MWCO	TMP (bar)	Cross-flow velocity (m/s)	Final or mean flux ($L/m^2 \cdot h$)	References
Acetic acid Vegetable processing Slaughterhouse	side-stream	0.2 µm	-	2-3	5-10	(Fuchs *et al.*, 2003)
Food industry	side-stream	20-70 kDa	2	1-1.1	10-30	(He *et al.*, 2005)
Soybean processing	side-stream	15 kDa	-	-	-	(Yushina and Hasegawa, 1994)
Brewery	side-stream	200 kDa	1.7-2.4	2.4-3.2	-	(Ince *et al.*, 2000; Ince *et al.*, 2001)
Brewery	side-stream	10 kDa	1-2		-	(Fakhru'l-Razi, 1994)
Brewery	side-stream	40 kDa	1.4–3.4	1.5–2.6	10-18	(Strohwald and Ross, 1992)
Potato starch bleaching	side-stream	0.1 µm	1	1.5-2	-	(Brockmann and Seyfried, 1996; Brockmann and Seyfried, 1997)
Palm oil mill	side-stream	200 kDa	1.5	2.3	26-31	(Fakhru'l-Razi and Noor, 1999)
Alcohol distillery	side-stream	20 kDa	1-2	0.24-0.95	3-10	(Choo and Lee, 1996b)

Table 1.2: Membrane performance of AnMBRs for wastewater treatment (continued)

Wastewater	Configuration	Pore size or MWCO	TMP *(bar)*	Cross-flow velocity *(m/s)*	Final or mean flux *(L/m²·h)*	References
Alcohol fermentation	side-stream	0.2 µm[a] 0.14 µm[b]	0.6	3	~115 ~75	(Kang *et al.*, 2002)
Molasses	UASB + submerged[c]	10 µm	-	-	40-60	(Hernandez *et al.*, 2002)
Wheat starch and gluten production waste	side-stream	0.2 µm	-	0.9	-	(Yanagi *et al.*, 1994)
Kraft bleach wastewater	side-stream	10 kDa	1.72	2.15	-	(Hall *et al.*, 1995)
Kraft pulp mill	side-stream[d]	0.16 µm	60	1.75	27	(Imasaka *et al.*, 1993)
Kraft pulp mill	side-stream	2000 kDa	-	-	-	(Minami *et al.*, 1991; Minami, 1994)
Sewage	submerged	0.03 µm	0.6		5-10	(Wen *et al.*, 1999)
Primary sludge	side-stream	60 kDa	2	4.5	120	(Ghyoot and Verstraete, 1997)
Primary sludge	side-stream	0.1 µm	1.1	2	25-42	(Murata *et al.*, 1994)

Table 1.2: Membrane performance of AnMBRs for wastewater treatment (continued)

Wastewater	Configuration	Pore size or MWCO	TMP (bar)	Cross-flow velocity (m/s)	Final or mean flux ($L/m^2 \cdot h$)	References
Heat treated sewage sludge	submerged	0.1 µm	0.27	0.2-0.3	2.5-8	(Kayawake *et al.*, 1991)
Macerated pig manure	side-stream	40 kDa		1.5-3.5	20-40	(du Preez *et al.*, 2005)
Swine manure	side-stream	20 kDa	0.3-0.7	1-2	5-10	(Padmasiri *et al.*, 2007)
Cow manure	side-stream	0.2 µm		3.3	40-80	(Zitomer *et al.*, 2005)

MWCO stands for molecular weight cut-off
[a] organic membrane
[b] inorganic membrane
[c] module submerged on the top of an UASB reactor
[d] with gas slug flow-gaslift circulation (no liquid pumping)

1.6. Scope and outline of this thesis

The present thesis studied the application of AnMBRs for wastewaters treatment as a way to promote enhanced biomass retention. Emphasis was set to operation at high temperatures (55 °C) and at high salinity, conditions under which biofilm or granule formation does not proceed well. The biological capacity and the filtration performance of AnMBRs were thoroughly studied, under a wide variety of conditions. The thesis analyses the technical feasibility of the application of membrane filtration to anaerobic digestion, and comments on the economy of AnMBR systems.

In Chapter 2 the phenomenon of cake formation is studied, when applying a submerged configuration using tubular microfiltration membranes. The effect of biomass concentration and gas flow rate on the critical flux and supra-critical cake formation rate is analysed, both under mesophilic and thermophilic conditions.

Since first introduced by Field *et al.* (1995), the critical flux has turn into a useful concept, since operation under sub-critical conditions usually results in long term operation, without the need of membrane cleaning operations. Chapter 3 describes the development of an on-line tool to control the applied flux or other operational conditions, in order to keep reactor operation in the range of the critical flux. For this purpose, a mathematical tool for steady-state analysis is proposed to analyse the TMP evolution.

Chapters 4 and 5 deal with the application of a submerged AnMBRs for wastewater treatment, using tubular microfiltration membranes. Chapter 4 focuses on mesophilic conditions, with emphasis on the study of cake formation and how this phenomenon can limit the applicable flux. Chapter 5 deals with the application of thermophilic submerged MBRs. In the latter case, factors affecting long term operation are identified and evaluated, using acidified and non-acidified substrates as feed. A comparison with mesophilic conditions is also performed.

The application of AnMBRs for the treatment of wastewaters containing a high fraction of particulate organic matter is studied in Chapter 6. Both mesophilic and thermophilic conditions were considered.

Chapter 7 evaluates the feasibility of applying high cross-flow liquid velocities as a way to control particle deposition in thermophilic AnMBRs. Two side-stream cross-flow thermophilic AnMBRs were operated for this purpose, with completely acidified and non acidified synthetic substrates. The effects of high shear stress promoted by the cross-flow operation on the physical and biological properties of the biomass were studied. In addition, the effect of the degree of substrate acidification on the system performance was also assessed.

The effect of membrane based biomass retention on the treatment of a synthetic acidified wastewater under extreme saline conditions is analysed in Chapter 8. The amount and activity of retained biomass in an AnMBR is evaluated in comparison with that achieved in a UASB reactor, during long term operation.

Finally, Chapter 9 concludes the thesis with a general discussion.

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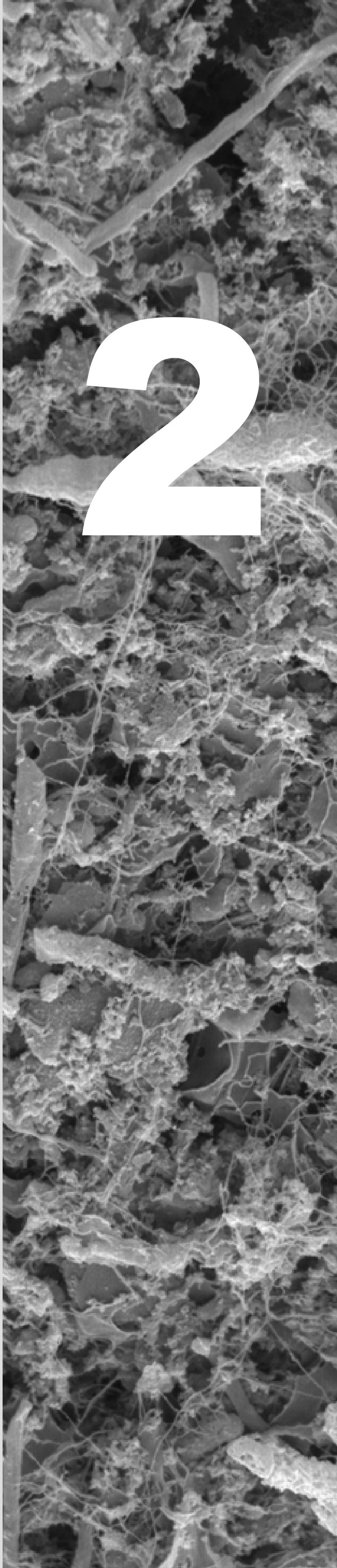


Cake layer formation in anaerobic submerged membrane bioreactors (AnSMBR) for wastewater treatment

Abstract

Cake layer formation in anaerobic gas-sparged submerged membrane bioreactors was studied using the critical flux concept, at 30 °C and 55 °C. The impact of biomass concentration and superficial gas velocity on cake layer formation was studied, using response surface methodology. Under mesophilic conditions, assessed critical flux values were in the range 5-21 L/m²·h, while a first order relation between critical flux and both biomass concentration and gas flow rate was observed. Within studied range of experimentation, at 30 °C, the effect of biomass concentration on critical flux was three times higher than the effect of gas superficial velocity. Under thermophilic conditions, critical flux values were in the range 16-23 L/m²·h, even though gas superficial velocities were about 50% lower than in the mesophilic reactor. At 55 °C, both biomass concentration and gas superficial velocity presented a value, below and over which no further effect on critical flux was observed. On a short term basis (minutes or hours), cake layer formation was mainly reversible. However, cake layer formation proceeds fast once critical flux has been exceeded, restricting feasible operational flux to the range of the critical flux.

2.1. INTRODUCTION

Anaerobic process had been successfully used for the treatment of wastewaters during the passed decades. Nowadays, it can be considered an established technology and it is successfully used for the treatment of many kinds of industrial wastewaters as well as sewage. It offers the possibility of an efficient treatment with low operational costs (Lettinga *et al.*, 1997). The success of anaerobic wastewater treatment can be attributed to an efficient uncoupling of the solids residence time from the hydraulic residence time through biomass retention, which is usually accomplished through biofilm or granule formation. With this strategy, a high concentration of biocatalyst is obtained, leading to high volumetric treatment capacities.

In situations where biofilm or granule formation cannot be guaranteed, such as extreme salinity and high temperatures, or when complete biomass retention must be ensured, membrane assisted physical separation can be used to achieve the required sludge retention. Membrane bioreactors (MBR) ensure biomass retention by the use of micro or ultra filtration modules. Since biomass is physically retained inside the reactor, there is no risk of cells washout and the sludge retention is non-dependent on the formation of biofilms or granules.

Membrane fouling is definitively the main drawback of the application of membrane bioreactors for wastewater treatment (Flemming *et al.*, 1997). Membranes themselves represent a relevant capital cost, so everything that can reduce their lifetime will affect directly the process economics. Moreover, membrane cleaning affects reactor operation due to the need of installation stoppage, produces chemicals that need to be disposed, and may affect membrane properties and lifetime. Numerous factors have been identified as flux decline promoters, such as biomass, colloids (Choo *et al.*, 2000), soluble organic matter (Harada *et al.*, 1994), inorganic precipitates (Choo and Lee, 1996; Yoon *et al.*, 1999) and extra-cellular polymers (Nagaoka *et al.*, 1996; Chang and Lee, 1998). The relative importance of each one of these agents will depend on the imposed operational conditions. Considering the low growth rates of anaerobic bacteria, anaerobic membrane bioreactor (AnMBR) technology is likely to be only feasible if the systems can be operated at high biomass concentration. This would enable high volumetric loading rates, and therefore small reactors volumes. However, solids concentration directly impacts convective flow of particles towards the membrane surface. Therefore, solids deposition over the membrane is likely to be the most important factor limiting the critical flux in AnMBRs.

Solids deposition in MBRs is usually controlled by inducing surface shear. In submerged MBRs this is usually accomplished by gas sparging for which, in AnMBRs, the produced biogas can be recirculated. The applied gas flow represents an important operational parameter for controlling cake layer development, but will affect energy requirements for the applied system.

In the present chapter, the phenomenon of cake layer formation on membrane surfaces in anaerobic submerged membrane bioreactors (AnSMBR) is studied. The effect of permeate flux, gas sparging, solids concentration and temperature is evaluated. The critical flux concept is used to define the flux at which noticeable cake layer formation begins to take place.

2.2. MATERIALS AND METHODS

2.2.1 Reactors setup

Cake layer formation was studied using two laboratory scale AnSMBRs. Reactors were 3.7 L of useful volume, fitted with tubular polysulphone microfiltration membranes with a mean pore size of 0.2 µm (Triqua, The Netherlands). Reactors were operated under thermophilic (55 °C) and mesophilic (30 °C) conditions. Membrane modules were composed of 4 tubes of 36.7 and 0.9 cm of length and diameter, respectively. Each module had a membrane area of 0.042 m^2. Gas sparging was used to provide mixing and to control solids deposition over the membrane surface. In order to increase liquid and gas superficial velocities in the vicinity of the membranes, digesters were operated as gas-lift reactors, with the membrane modules placed inside the riser. Gas superficial velocity (V_G) was evaluated considering the free transversal area of the riser. Biogas was recirculated by means of compressors (KNF N810FT.18, Germany). Gas flow rates were measured using variable area rotameters (Brooks Instrument R2-15-A, The Netherlands). Permeate was collected by means of peristaltic pumps (Watson Marlow 323U, UK), that provided the required trans-membrane pressure (TMP). TMPs were measured by pressure sensors (AE Sensors ATM, The Netherlands) located in the permeate lines. Figure 2.1 presents a scheme of each reactor setup.

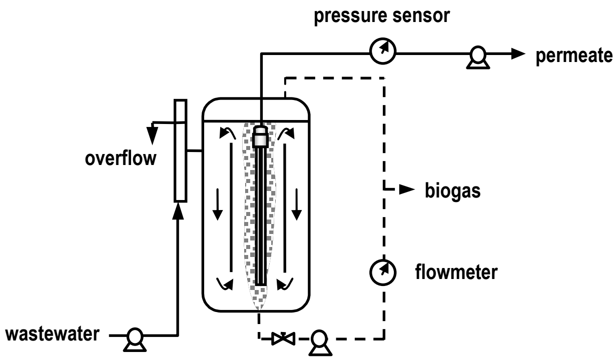


Figure 2.1. Schematic representation of AnSMBR setup. Doted lines indicate gas flows.

2.2.2 Membrane resistance determination

Membrane resistance was determined recording the TMP at increasing flux steps, in demineralised water. Flux steps were 5, 15 20 and 25 $L/m^2 \cdot h$. Each step was maintained for 5 minutes. Membrane permeability (Perm) is evaluated as the slope of the applied flux (J) at each step versus the mean TMP. Membrane resistance (R_M) is then reciprocally correlated to the permeability:

$$\mathrm{Perm} = \frac{J}{\mathrm{TMP}} \tag{1}$$

$$R_M = \frac{\mathrm{TMP}}{J \cdot \eta} = \frac{1}{\mathrm{Perm} \cdot \eta} \tag{2}$$

where η represents the permeate viscosity. The membrane was simply rinsed with clean water prior to resistance determination. Then the measured resistance represents the sum of the resistance of the membrane itself, plus the resistance due to fouling and stable cake formation, i.e. the one that cannot be easily reverted by back-flush cycles. This resistance is therefore referred to as apparent membrane resistance.

2.2.3 Critical flux measurement

The critical flux was determined applying a flux step method (Le Clech *et al.*, 2003). It consisted of successive filtration steps of 10 minutes, with flux increments of 2 $L/m^2 \cdot h$. One minute of back-flush was included between each cycle. Back-flush was applied by reversing the flow direction, keeping the flux at the same value than during filtration. Critical flux measurement automatically stopped when TMP reached 150 mbar. The critical flux was assumed to be exceeded when the slope of the TMP against time failed an hypothesis test, with null hypothesis dTMP/dt = 0 (Montgomery *et al.*, 2001). Significance level was 95%. Subsequently, the critical flux indicates the flux at which cake layer formation becomes noticeable.

2.2.4 Analyses

Biomass concentration was measured as total suspended solids (TSS) and volatile suspended solids (VSS), determined according to Standard Methods (APHA *et al.*, 1998). Permeate viscosity was determined using an Ubbelohde viscometer (Tamson instruments, The Netherlands). Sludge particle size distribution was measured by laser diffraction analysis (Coulter LS230, Beckman Coulter, USA). Particle size data is presented based on volume distributions.

2.2.5 Reactors start-up

Crushed anaerobic granular sludge was used as source of inoculum. Granules were mechanically crushed using a blender. The thermophilic reactor was inoculated with sludge that had been previously acclimated to thermophilic conditions in an UASB reactor, for a period of 3 months. Reactors were fed with a synthetic wastewater based on a volatile fatty acids (VFA) mixture as chemical oxygen demand (COD) source. The acetate:propionate:butyrate ratio in the mixture was 2:1:1, expressed as COD. Inlet COD concentration was 5 g/L. During the start-up, the organic loading rate was increased by reducing the hydraulic retention time, up to a loading rate of 20 and 15 g COD/L·d, for the thermophilic and mesophilic reactors respectively. Start-up procedure took 75 days. The reactors were operated with a cycle consisting of 10 minutes of filtration, followed by 30 seconds of back-flush.

2.2.6 Bubble size influence on critical flux

In order to evaluate the influence of bubble size on filtration performance, the thermophilic reactor was operated using either a coarse or a fine diffuser. Critical flux measurements were performed with each diffuser at V_G values of 18, 36 and 54 m/h. The fine diffuser was a 4 cm diameter glass filter, while the coarse diffuser was a 3 cm plastic cap fitted with seven 1.5 mm perforations. The effect of the bubble diffuser on cake formation when operating over critical flux was also studied, analysing the TMP increase over time. During these critical flux measurements, biomass concentration was set at 40 g TSS/L. Bubble sizes were estimated using image analysis, when testing the diffusers in clean water.

2.2.7 Effect of biomass concentration and V_G on critical flux

Response surface statistical experimental design was used to evaluate the effect of V_G and biomass concentration on the critical flux. The critical flux was measured at different values of V_G and sludge concentration, using a face centred central composite design for two factors (Montgomery, 2001). This experimental design was chosen, since it only requires three levels for the studied factors. The centre point was replicated 4 times in order to estimate the variance of the response. Experiments were carried out in the mesophilic and in the thermophilic reactor. The studied biomass concentrations were 25, 37.5 and 50 g TSS/L, which were chosen to place the centre point in the same range of total solids concentration of sludge bed reactors. Corresponding VSS concentrations were 17.4, 26.1 and 34.8 g/L for the mesophilic reactor; and 16.9, 25.3 and 33.7 g/L for the thermophilic reactor. Differences between mesophilic and thermophilic VSS concentrations were the result of different sludge ash contents. The applied V_G values were 35, 53, 70 m/h for the mesophilic reactor and 12, 27, 42 m/h for the thermophilic reactor. The levels for the thermophilic MBR were selected based on previous experiments (data not shown), which showed that further increases in V_G over 42 m/h did not produce important changes in critical flux. Changes in biomass concentration were produced by either dilution with a 2 g/L sodium bicarbonate solution in tap water, or by concentration through membrane filtration, using a membrane with the same properties that the one used to carry out the experiments. The membranes were flushed with demineralised water between each critical flux determination. Membrane resistance was measured before each critical flux analysis to verify that no irreversible fouling had occurred during previous determinations, assuming uniform membrane quality throughout the experiments.

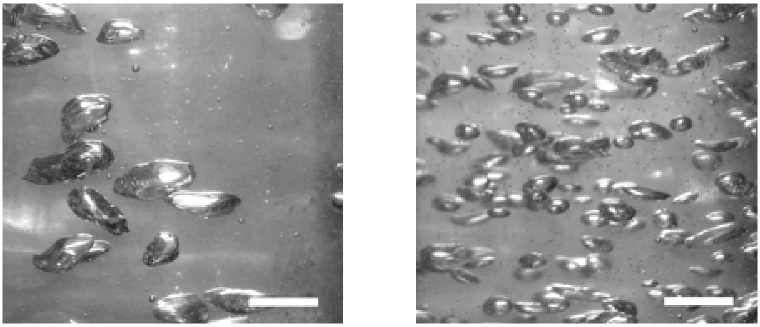
2.2.8 Cake formation reversibility

The reversibility of TMP increase due to cake formation was tested in both reactors through cyclic step variations in flux. The flux was increased in successive filtration steps of 25 minutes. Once an important cake layer formation was observed, which was indicated by a TMP over 200 mbar, the flux was reduced following the same flux steps, but now in the reverse direction. Two gas flow rates were tested in each reactor, in the presence and absence of a 30 seconds back-flush between each filtration cycle. As during the critical flux measurements, back-flush was applied by reversing the flow direction, keeping the flux at the same value than during filtration. The biomass concentration was fixed at 40 g TSS/L during these experiments.

2.3. RESULTS AND DISCUSSION

2.3.1 Effect of diffuser type

Figure 2.2 presents pictures of the bubbles generated by each diffuser, in clean water. Mean equivalent bubble diameter for the fine diffuser was 2.9 mm, with a standard deviation of 0.5 mm. Mean equivalent bubble diameter for the coarse diffuser was 7.0 mm, with a standard deviation of 1.4 mm. When tested in clean water, the coarse diffuser achieved bubbles with diameters twice as big as the fine diffuser. The presence of solutes and solids will change liquid density and surface tension, affecting bubble size formation and coalescence (Gurol and Nekouinaini, 1985). Therefore bubble sizes are likely to be different during the actual reactor operation. However, clean water test provides a general idea about the differences in bubble sizes produced by the two diffusers.



Coarse diffuser **Fine diffuser**

Figure 2.2. Pictures of the bubbles generated by coarse and fine diffusers, in clean water. Bar indicates 10 mm.

Figure 2.3 presents the effect of the two tested gas diffusers on the critical flux, for the thermophilic reactor. An increase in critical flux is achieved when the coarse diffuser is used. The positive influence of switching from the fine to the coarse diffuser can be observed under all V_G values tested. Higher critical fluxes achieved with the coarse diffuser are probably related to the higher mixing and mass transfer levels that bigger bubbles can provide, as a result of a stronger bubble wake (Li *et al.*, 1997). Under the conditions of this study, an increase in V_G from 36 to 54 m/h produces the same increase in critical flux than the change of diffuser at a V_G of 36 m/h. Increments in critical flux due to the shift to the coarse diffuser are relatively small, between 10 and 15%. However, this increase represents an important process improvement, since the value of the critical flux is directly related with membrane requirement, which represents one of the main capital costs of submerged membrane bioreactors. The use of a coarse diffuser is also positive since it decreases the energy requirements due to the reduction of the pressure drop through the diffuser. Furthermore, the use of coarse diffusers reduces the chances of clogging, decreasing maintenance requirements.

Figure 2.4 presents the TMP increase rates, during the filtration cycles exceeding the critical flux. Results for V_G values of 18 and 54 m/h are presented, with both gas diffusers, as a function of the permeate flux. To facilitate comparison, the flux is presented as its difference with critical flux (J-J_C). TMP increase rates are higher for the fine diffuser, at both gas flow rates. Differences in TMP increase rates are between 30 and 65%, depending on the imposed flux and gas superficial velocity. Results show that the change in diffuser type is as effective in decreasing cake formation rate, as an increase in gas superficial velocity of close to 300%, i.e. from V_G 18 to 54 m/h.

Due to the higher critical fluxes, lower supra-critical fouling rates, and lower intrinsic energy requirements, coarse diffusers were selected and implemented in both reactors to proceed with the rest of the experiments.

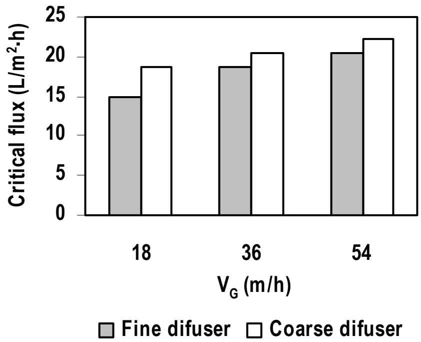


Figure 2.3. Effect of the gas diffuser type (coarse of fine) on the critical flux of the thermophilic AnSMBR, at three different values of V_G.

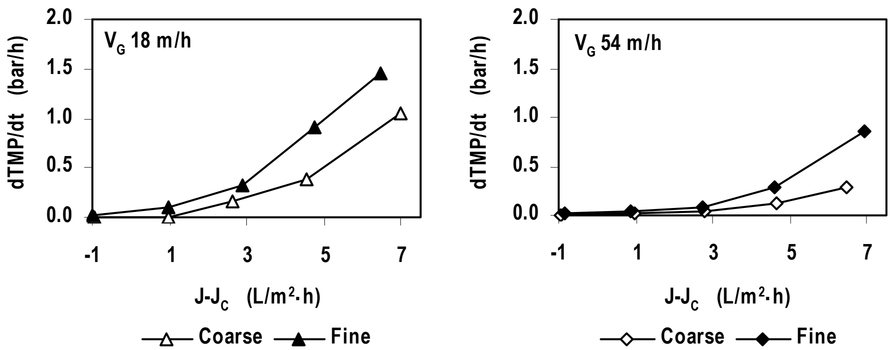


Figure 2.4. Effect of the gas diffuser type (coarse or fine) on the TMP increase rate when operating over critical flux, at two values of V_G: 18 and 54 m/h

2.3.2 Analysis of critical flux measurements

Figure 2.5A presents a typical TMP response curve, resulting from a stepwise flux increase during a critical flux measurement, in the mesophilic reactor. During the first stages of flux increase, TMP increments are linear (Figure 2.5B). However, at a specific flux, the resulting TMP deviates from the linear correlation and increases to higher levels. This deviation is caused by the formation of a cake layer over the membrane surface, indicating that the critical flux has been exceeded.

Figure 2.5B also shows the pressure at the end of each back-flush period, performed between each flux increase. It should be noted that the back-flush TMP shows a linear correlation with the imposed flux, which means a constant resistance. A constant resistance during the back-flush, even over the critical flux, indicates that the pressure increase during the filtration period was mainly the result of a reversible phenomena. Reversible cake formation over critical flux was observed under all tested conditions of gas flow rate and biomass concentration, for both mesophilic and thermophilic reactors.

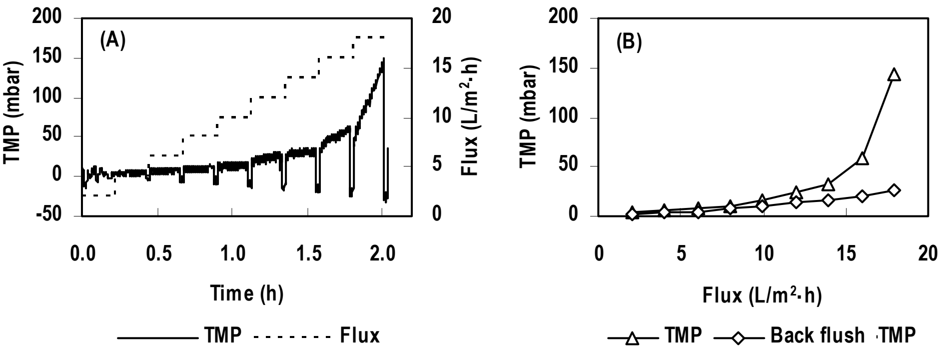


Figure 2.5. Typical critical flux measurement for mesophilic reactor: (A) Stepwise flux increase and TMP response evolution, (B) TMP at the end of each filtration and back-flush period. Experimental conditions: biomass concentration 37.5 g TSS/L, V_G 52.5 m/h.

2.3.3 Effect of biomass concentration and V_G on critical flux

Figure 2.6 presents the apparent membrane resistance before each critical flux determination of the central composite design, for each reactor. In each case, the analysis of variance (ANOVA) shows no statistical difference between the observed values, with a 95% confidence. This confirms that no significant irreversible fouling occurred during the experiments and that for each reactor all of the experiments were performed under similar conditions of membrane quality. The objective of this research was to study cake formation, since it is likely to be the main limiting factor for the application of anaerobic MBRs, if high biomass concentrations are considered. Apparent membrane resistance of the thermophilic reactor is clearly lower than that of the mesophilic reactor, due to different fouling rates during the start-up procedure. This difference in apparent membrane resistance does not prevent comparison between results from both reactors, since cake formation was the main phenomena observed during the experiments. Under cake formation conditions, membrane is covered by particles, and its properties do not determine at a high extent the dynamics of particle deposition.

Figure 2.7 shows the effects of V_G and biomass concentration on the critical flux. Under mesophilic conditions (Figure 2.7A), biomass concentration strongly affects the critical flux. The biogas sparging level also exerts a significant influence. An increase in biomass concentration will increase the convective flow of solids towards the membrane surface. On the other hand, an increase in V_G will increase shear rate, increasing the back-transport of solids from the membrane proximity. Therefore, an increase in solids concentration, and/or a decrease in V_G should decrease the critical flux. Figure 2.7A suggests a first order effect of both factors, without any significant interaction between them. The application of the stepwise regression method for variable selection (Montgomery, 2001) clearly showed that only the first order terms of a second order linear regression model have statistical significance (95% confidence level). No significant interaction between the influences of V_G and biomass concentration was detected, under mesophilic conditions. This means that in the studied range both effects are independent. Results show that biomass concentration exerts a higher effect on the critical flux, close to 3 times higher than the effect of V_G, under the selected range of experimentation. Therefore, sludge concentration is the main operational parameter for cake layer formation in a mesophilic AnSMBR.

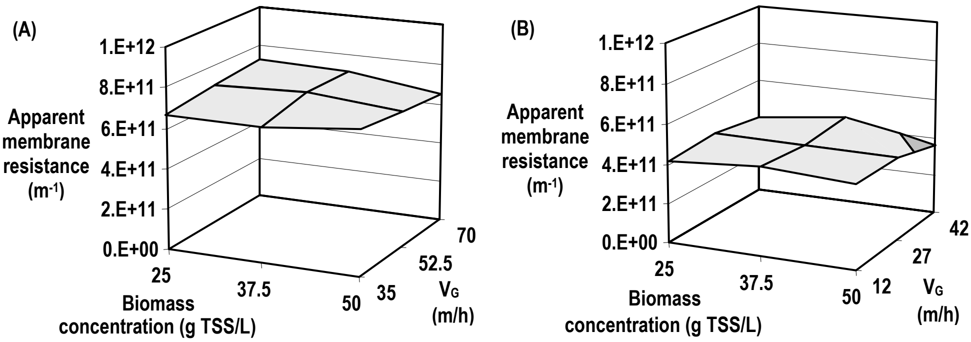


Figure 2.6. Apparent membrane resistance prior to each critical flux measurement of the central composite design. (A) Mesophilic reactor, (B) thermophilic reactor.

The situation of the thermophilic reactor was different, as can be seen in Figure 2.7B. Critical flux values were higher than those for the mesophilic reactor. Moreover, in the range of experimentation, the tested factors did not showed a first order response, as was the case of the mesophilic reactor. The relation between biomass concentration and critical flux in the thermophilic reactor suggests the existence of a sludge concentration below which no big changes in critical flux occurs. This value seems to be around the centre point. A similar behaviour was observed for V_G, since its effect on the critical flux decreases at higher values. In fact, several studies performed with aerobic MBRs have pointed out the existence of a certain gas aeration intensity over which no further improve in fouling control can be achieved (Ueda *et al.*, 1997; Liu *et al.*, 2000; Sofia *et al.*, 2004). Over this gas flow rate no further increases in surface shear can be accomplished. Apparently, this gas flow rate was not reached under the experimentation range selected for the mesophilic reactor. However, it was indeed reached under thermophilic conditions, despite the fact that gas superficial velocities in the thermophilic reactor were much lower than in the mesophilic reactor.

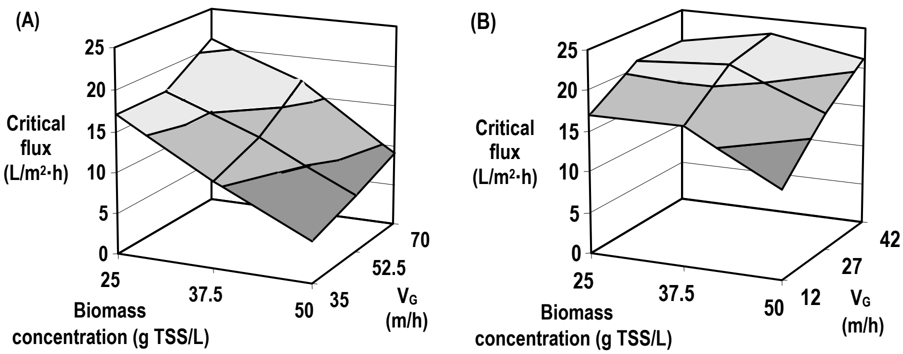


Figure 2.7. Effect of biomass concentration and V_G on the critical flux: surface respond methodology. V_G values were evaluated considering the free transversal area of the riser. (A) Mesophilic reactor, (B) thermophilic reactor.

Figure 2.8 presents the sludge particle size distributions of both reactors. No big differences can be observed. The thermophilic distribution shows the presence of particles slightly smaller than the mesophilic reactor. A smaller particle size distribution could result in lower critical fluxes since hydrodynamic back-transport of particles is positively related with particle size (Tardieu *et al.*, 1998). Since the critical flux in the thermophilic reactor is higher, the observed difference in particle size distribution is not likely the cause for the differences observed between the behaviour of both reactors.

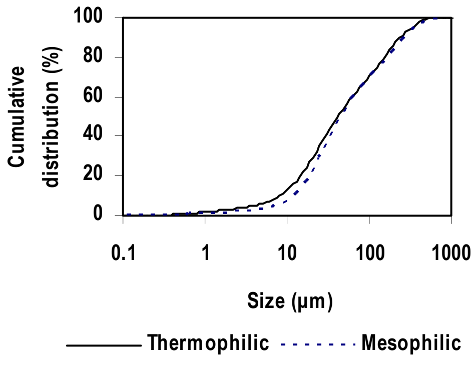


Figure 2.8. Cumulative particle size distribution of the sludge from the AnSMBRs.

Higher critical fluxes of thermophilic reactor are more likely related with different values of sludge viscosity and its effect on the acting forces over particles in suspension. Particle deposition over the membrane surface is determined by the balance of forces that a particle experiences towards and away from the membrane. Permeation flux results in a drag force towards the membrane. A reduction in viscosity will produce a decrease in this drag force (Altmann and Ripperger, 1997). On the other hand, three back-transport mechanisms have been identified on cross flow microfiltration: Brownian diffusion, shear induced diffusion and inertial lift. All of them predict an increase in long term flux when reducing suspension viscosity (Belfort *et al.*, 1994). This means that a decrease in viscosity will have then a double effect, decreasing drag force and enhancing back-transport mechanisms, resulting in a higher net force away from the membrane surface. This will reduce particle deposition and therefore increase the critical flux. Particle deposition is determined by conditions in the proximity of the membrane surface. These conditions are different than in the bulk of the suspension, due to the concentration polarization effect (Belfort *et al.*, 1994). Therefore, estimation of the exact effect of temperature on viscosity, and thus on the balance of forces acting over the particles, is complex. Nevertheless the viscosity will certainly play a role and may partly explain the differences observed in Figure 2.7.

2.3.4 Cake formation over critical flux

Operation below the critical flux is a normal practice, since it enables long term operation in absence of membrane cleaning. Anyhow, field conditions may require in some occasions increases in the permeate flux. This may result in operation over the critical flux for some periods of time. Operation over critical flux inevitably implies cake formation. The rate of cake formation and therefore TMP increase will determine to what extent operation over the critical flux would be feasible. A direct way to report cake formation rates in MBRs is through the rate of TMP increase in time, i.e. dTMP/dt, during each filtration step. However, direct comparison of cake formation rates expressed in the latter way can be misleading. The fouling rates determined during the critical flux measurements were obtained at different flux values, and different biomass concentrations. These are parameters that affect the convective flow of particles towards the membrane surface. A more objective comparison can be made if filtration resistances are taken into account. The filtration resistance relates filtration flux with the actual TMP. The filtration resistance can be divided in two terms, i.e. apparent membrane resistance (R_{MAp}) and cake resistance (R_C), giving:

$$J = \frac{1}{A}\frac{dV}{dt} = \frac{TMP}{\eta}\frac{1}{R_{MAp} + R_C} \qquad (3)$$

where A represents the membrane area, V the permeate volume, and t the time. R_{MAp} represents the apparent membrane resistance at the time of the experiments (presented in Figure 2.6). Others partial resistances, like pore blocking for example, were not considered in this analysis, since cake formation was the main reason for TMP increase. R_C depends on the extent of particle deposition over the membrane surface. If a dead end filtration process is considered, in absence of any back-transport, cake resistance can be expressed as a function of the specific cake resistance (α), the solids concentration (C) and permeate volume (Perry and Green, 1999):

$$R_C = \frac{V}{A}\alpha \cdot C \qquad (4)$$

Equation 4 needs to be corrected to include the cross-filtration effect, introducing the factor K (Cho *et al.*, 2004):

$$R_C = \frac{V \cdot K}{A} \alpha \cdot C \tag{5}$$

The inclusion of K is required since in cross-flow microfiltration not all the particles are subjected to deposition over membrane surface, as is the case of dead end filtration. This is due to back-transport induced by cross-flow operation. Therefore, for a dead end filtration process K=1. Under sub-critical conditions K=0, i.e. no cake formation takes place. If R_C of equation 5 is substituted in equation 3, and a constant flux is considered, we obtain:

$$TMP = \frac{\eta \cdot K \cdot \alpha \cdot C \cdot J}{A} V + \eta \cdot R_{MAp} \cdot J \tag{6}$$

Subsequently, for a constant flux filtration, a plot of TMP against permeate volume will yield a straight line, if no important levels of cake compression or irreversible fouling occurs. Since flux, permeate viscosity, membrane area and solids concentration are constant and known during each step of the critical flux determinations, the slope of a TMP versus permeate volume chart can be used to determine the factor $\alpha \cdot K$. Because specific cake resistance is unknown, K cannot be independently evaluated. However, the product $\alpha \cdot K$ is regarded a useful parameter to evaluate or compare cake formation phenomena under the different conditions applied. The effect of cake formation on TMP will depend on two factors: the deposited solids resistance, represented by α; and the amount of deposited solids, determined by the cross flow effect which is represented by K. Figure 2.9 and Figure 2.10 represent the cake development using the parameter $\alpha \cdot K$. To facilitate comparison the flux is presented as its difference with critical flux. The graphs also include the last step before the critical flux has been reached.

Figure 2.9 reflects a strong influence of solids concentration on the product $\alpha \cdot K$, showing that biomass concentration is a key parameter during cake formation in mesophilic AnSMBRs. Doubling the biomass concentration (from 25 to 50 g/L), increments the $\alpha \cdot K$ product in one order of magnitude. At 50 g TSS/L, and at a flux only 3 $L/m^2 \cdot h$ higher than the critical flux, $\alpha \cdot K$ values are in the range of $1 \cdot 10^{14}$ m/kg. This means a TMP increase rate of around 1 bar/h. The changes in convective flow of particles towards the membrane due to different fluxes and biomass concentrations have been already accounted in the evaluation of $\alpha \cdot K$. Differences may be the result of changes in either K, α or both. An increasing sludge viscosity at higher sludge concentrations is expected to reduce particle back-transport (Belfort *et al.*, 1994). The latter will produce an increase in the parameter K at increasing sludge concentrations. This change in back-transport due to viscosity may also have lead to a preferential deposition of smaller particles, changing the value of α. Further research is needed in order to elucidate the impact of sludge concentration on the parameters α and K. Figure 2.9 also shows the effect of V_G on $\alpha \cdot K$. The impact of the gas superficial velocity is much smaller than that of the biomass concentration. The latter is considered the key operational parameter determining the feasibility of AnSMBR, since in addition to its impact on the cake layer formation, the applied sludge concentration also defines the volumetric loading capacity of the reactor.

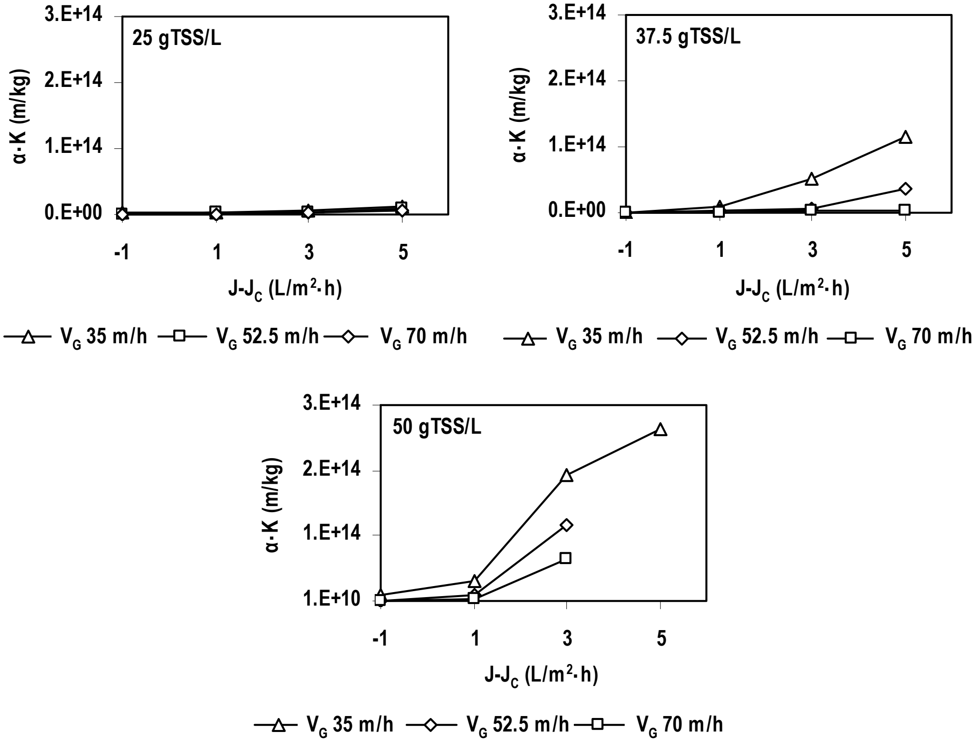


Figure 2.9. α·K product in the mesophilic reactor, versus the difference between flux and critical flux (J-J_C), at different values of V_G and biomass concentration.

Under thermophilic conditions, biomass concentration had almost no effect on α·K, as shown in Figure 2.10. It is inferred then that biomass concentration does not affect back-transport efficiency or specific cake resistance. As expected, in both reactors an increase in V_G reduces the cake formation rate. At a biomass concentration of 50 g TSS/L, the value of α·K at a V_G of 27 m/h was slightly higher than that at 42 m/h. This is probably the result of experimental error. It should be remembered that critical flux determination was performed based on steps of 2 L/m²·h. This imprecision is then likely to be the reason for this discrepancy. At thermophilic conditions, cake formation rates are smaller than those at mesophilic conditions. Anyhow, for both temperature conditions, the cake formation proceeds fast, when critical flux has been exceeded. At 55 °C, values of TMP increase rate where close to 0.5 bar/h at a flux only 3 L/m²·h higher than the critical flux. Observed values of TMP increase rate when operating over the critical flux severely restricts operational flux to the range of the critical flux, under both mesophilic and thermophilic conditions.

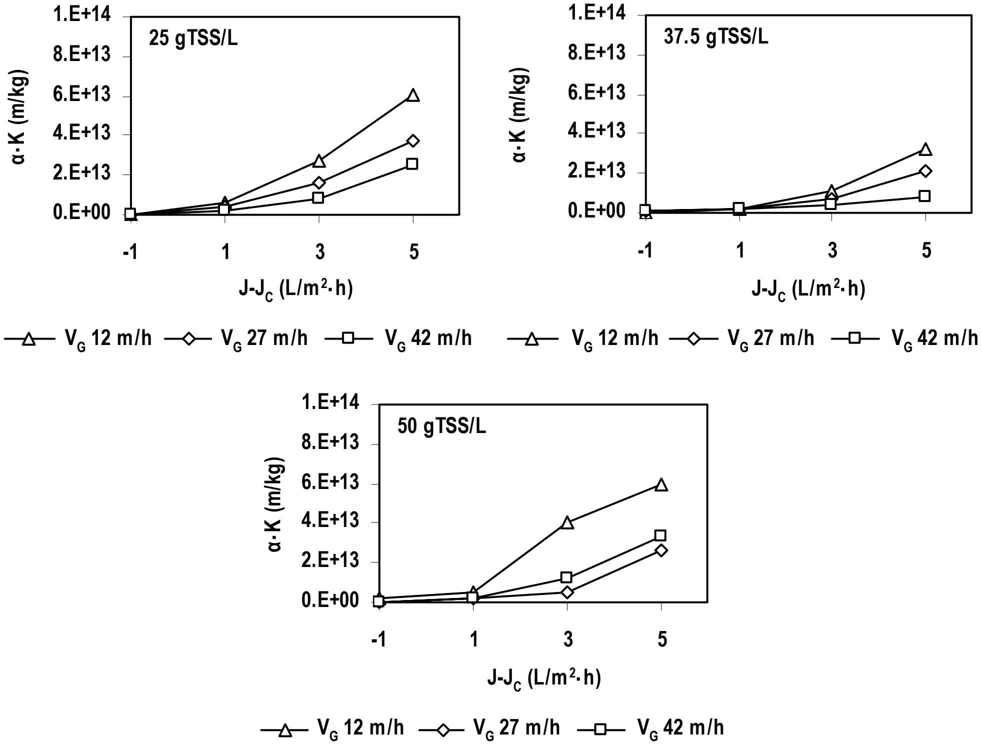


Figure 2.10. α·K product in the thermophilic reactor, versus the difference between flux and critical flux (J-J$_C$), at different values of V_G and biomass concentration.

2.3.5 Cake formation reversibility

Figure 2.11 and Figure 2.12 present the results of the experiments performed to determine the degree of cake formation reversibility. In all cases the critical flux was exceeded and a cake layer was formed. A significant level of hysteresis is evident, in absence of back-flush, especially for the thermophilic reactor at low gas flow rate. Results show that the differences between the observed TMPs during the increasing and decreasing flux steps are reduced as the flux decreases. During the decreasing flux steps performed below the critical flux, no further deposition of particles takes place. Furthermore, TMP decrease during decreasing flux steps show that some detachment of the cake layer occurred. This is in agreement with observations from SiHassen *et al.* (1996) and Defrance and Jaffrin (1999) which indicate the existence of a threshold shear rate necessary for cake detachment. Due to the action of adhesive forces on deposited particles, individual particle attachment to the cake layer and/or membrane surface generally is an irreversible process. Cake layer removal takes place by removing large agglomerates or layer fragments (Altmann and Ripperger, 1997).

The inclusion of a 30 seconds back-flush between the filtration cycles is highly efficient in removing the cake layer in mesophilic and thermophilic reactors. Experiments with back-flush show no apparent hysteresis, showing that cake layer deposition at fluxes exceeding the critical flux is a mostly reversible process in both reactors. This is in agreement with the first order linear relation between back-flush TMP and flux observed during each critical flux determination (Figure 2.5B). It must be noted that the obtained results account for short term effects. In a long term experimental run (several months), cake consolidation may happen, affecting reversibility.

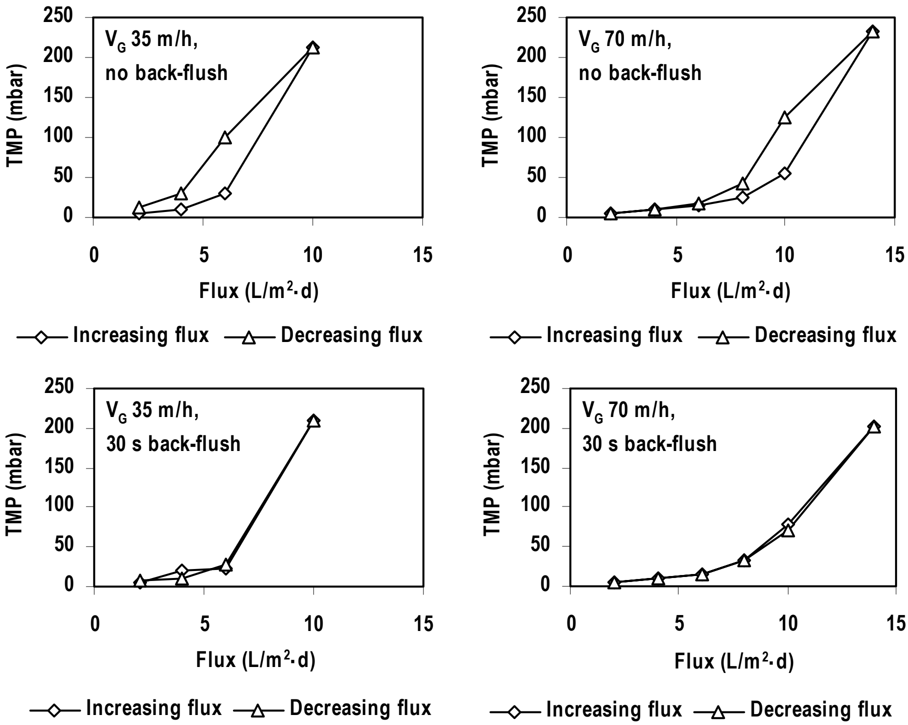


Figure 2.11. Step increase and decrease of flux to test cake formation reversibility in the mesophilic reactor. The pressure at the end of each filtration cycle against the flux is presented.

Results show the feasibility of AnSMBR systems, which are operated at sludge concentrations 3-5 times higher than comparable aerobic MBR systems. The observed critical flux values are in the range of 20 $L/m^2{\cdot}h$, agreeing with values observed under aerobic conditions (Stephenson *et al.*, 2000). Our results clearly show that for mesophilic and thermophilic conditions cake formation on the membrane surface is the key limiting phenomenon in AnSMBRs. Thermophilic conditions resulted in higher fluxes, and thus higher hydraulic capacities, even when operated at lower gas superficial velocities. At high temperatures, i.e. 55 °C, the critical flux was less affected by operational conditions, such as gas sparging and biomass concentration, in comparison with the mesophilic reactor. This means lower energy requirements and a higher conversion capacity. Under thermophilic conditions, the level of cake formation when operating over the critical flux was found to be less, resulting in a more stable operation, even though thermophilic reactor was operated at lower values of V_G.

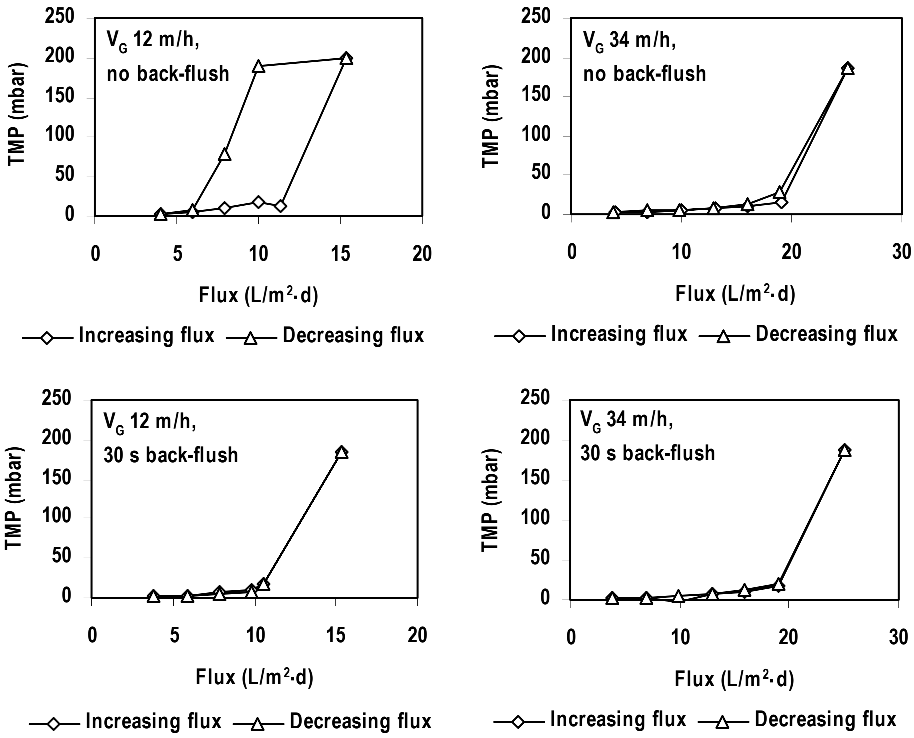


Figure 2.12. Step increase and decrease of flux to test cake formation reversibility in the thermophilic reactor. The pressure at the end of each filtration cycle against the flux is presented.

2.4. CONCLUSIONS

The effect of biomass concentration and gas flow rate on cake formation was studied, in AnSMBRs. Biomass concentration showed to be an important factor determining cake formation in mesophilic MBRs. Under mesophilic conditions, biomass concentration affects linearly critical flux. An increase from 25 to 50 g TSS/L reduces critical flux from 21 $L/m^2{\cdot}h$ to 9 $L/m^2{\cdot}h$, at a V_G of 70 m/h. Even though gas sparging level also influences critical flux, its effect is much smaller than biomass concentration.

Thermophilic operation reduces drastically the effect of biomass concentration and gas sparging on cake layer formation, in comparison with mesophilic conditions. Biomass concentration and gas superficial velocity presented a value, below and over which no further effect on critical flux was found. In addition, thermophilic MBR required much lower levels of gas sparging in comparison with mesophilic MBR. For achieving similar levels of effluent flux at a fixed biomass concentration, gas requirements under thermophilic conditions were below 50% of those required for mesophilic conditions.

Even though cake formation showed to be mainly reversible in short term experiments, particle deposition proceeds fast once critical flux has been exceeded. At 50 g TSS/L, a flux increase of only 3 L/m^2·h over the critical flux results in a TMP increase rate of over 1 and 0.5 bar/h for the mesophilic and thermophilic reactors, respectively. The operational flux is, therefore, likely to be restricted to values close to the critical flux for both temperatures.

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3

On-line cake layer management by trans-membrane pressure steady state assessment in anaerobic membrane bioreactors for wastewater treatment

Abstract

Membrane bioreactors (MBR) have been increasingly applied for wastewater treatment during the last two decades. High energy requirements and membrane capital costs remain as their main drawback. A new strategy of operation is presented based on a continuous critical flux determination, preventing excessive cake layer accumulation on the membrane surface. Reactor operation is divided in cycles of 500 seconds filtration followed by a short back-flush of 15 seconds. If cake layer formation is detected during continuous operation, a decrease in flux or an increase in cross flow velocity is performed. The proposed approach keeps reactor operation oscillating around the critical flux, minimizing reactor maintenance and maximizing performance. An easy to operate statistical steady state determination tool for the trans-membrane pressure was used to detect cake layer formation. The developed control approach was tested on two anaerobic MBRs equipped with submerged membranes. Despite the existence of very different critical fluxes and cake layer formation characteristics, proposed approach was able to keep pressure increase during filtration cycles below 20 mbar. The developed approach is an efficient tool for on-line control of cake layer formation over the membranes, changing cross flow velocities by manipulating gas sparging in submerged MBRs.

3.1. INTRODUCTION

The conversion capacity of biological reactors is generally related with biomass concentration. Therefore, cells concentration is generally a key operational parameter. This, obviously, is also the case in biological wastewater treatment. Membrane assisted separation represents a reliable alternative to control cell retention, and it has been increasingly applied to wastewater treatment during the last two decades. In membrane bioreactors (MBR) microorganisms are physically retained inside the reactor, and a complete uncoupling of solids and hydraulic retention times can be then achieved.

So far, the main drawback of MBR systems is related with membrane costs and fouling (vanDijk and Roncken, 1997; Choo et al., 2000). Sub-critical flux operation has been regarded as an efficient way to control fouling and to achieve long term operation in absence of chemical cleaning or maintenance (Howell, 1995). Under sub-critical conditions, an equilibrium is established between the incoming particles moving towards the membrane by convective flow, and returning particles moving away from the membrane, due to back-transport. Pressure increase at constant flux operation can be easily applied for critical flux determination in any type of membrane process. Furthermore, in most applications the complete absence of fouling is not required. For these reasons, the weak definition of critical flux and its determination by pressure increase represents a valuable and practical tool for full-scale applications.

Critical flux assessment is usually based on short term experiments (Le Clech et al., 2003). Therefore, the critical flux is generally determined by the formation of cake layers. Cake formation over the membrane is one of the most important causes for flux decline in MBRs. This is certainly true for MBRs operated at high biomass concentrations, like wastewater treatment MBRs. Considering the low growth rates of anaerobic bacteria, biomass cake formation will particularly limit the operation of anaerobic MBR, since they are likely to be only feasible if the systems can be operated at high biomass concentrations.

Critical flux and cake formation rate over critical flux are functions of the hydraulic conditions, and therefore depend on the gas sparging rate and liquid superficial velocity in submerged and side-stream MBRs respectively (Bouhabila *et al.*, 1998; Howell *et al.*, 2004; Germain *et al.*, 2005). Therefore, in submerged MBRs, the gas flow can be used as a tool to dynamically control the critical flux in the range of the actual operational flux. So, in the same way that a critical flux can be asses at a certain gas flow rate, a critical gas flow rate can be identified for a certain permeate flux. The critical gas flow rate represents then the gas flow rate which is required to match the critical flux with the effective applied flux. The same definition can be applied to the liquid cross flow velocity in side-stream MBRs.

For practical purposes, full scale MBRs must be able to handle highly dynamic conditions, such as changes in wastewater flow and concentration. Therefore, dynamic flux assessment is a pre-requisite for stable reactor operation at the highest possible performance. The later demands a robust, reliable and plain tool, enabling on-line identification of critical conditions for process optimization. Such a tool would enable the dynamic control of gas sparging in submerged MBRs or superficial velocity in side-stream MBRs, to the minimum levels that provides absence or minimal cake layer formation, therefore minimizing energy requirements.

In the present work we present a novel and simple operation strategy that enables the detection of cake layer formation through pressure evolution. It can be easily used in combination with simple control strategies to minimize cake layer development and energy requirements. The proposed approach uses a mathematical tool for steady-state assessment in order to identify pressure increase at constant flux operation.

3.2. MATERIALS AND METHODS

3.2.1. On-line critical flux determination

The on-line critical flux determination is based on the analysis of the trans-membrane pressure (TMP) evolution in time. Accordingly to the weak definition of the critical flux, a flux is below the critical value if the reactor is operated at a constant flux and constant TMP. If, however, an increase in TMP is detected, then the critical flux has been exceeded. The steady state mathematical tool developed by Cao and Rhinehart (1995) was used to determine increments in TMP. The method uses the R statistic, a ratio of two different estimates of the variance of a time series of data. One is evaluated computing the differences of the data with respect to the average. The second uses mean squared differences of successive data. The ratio R will be near to 1 if the studied process variable is in steady state, i.e. the process mean is constant, and the additive noise is independent and identically distributed. If the process variable mean changes, then R will be over 1 (Cao and Rhinehart, 1995). Table 3.1 presents the equations required to compute R. Statistic parameters λ_1, λ_2, λ_3 where empirically chosen based on experimentation, to minimize type errors I and II (Montgomery, 2001). Critical values for R were selected according to the recommendations by Cao and Rhinehart (1997). Data sampling for the evaluation of the R-statistic was chosen to ensure the absence of autocorrelation. Data autocorrelation was determined evaluating the autocorrelation coefficient at different lag values (Box et al., 1978):

$$r_k = \frac{\sum_i (x_i - \bar{x})(x_{i+k} - \bar{x})}{\sum_i (x_i - \bar{x})^2} \quad (1)$$

where k represents the lag. The described steady state tool was selected for TMP increase identification since it is plain, robust and computational inexpensive. Indeed the method requires only simple calculations, and only 3 variables need to be stored for the next calculation step. Other methods like slope hypothesis tests are usually applied off-line, since they require considerable data storage, computational effort and user expertise.

3.2.2. Reactors setup

The on-line control strategy was tested in the anaerobic submerged membrane bioreactors (AnSMBR) already described in Chapter 2. Figure 3.1 presents a scheme of one reactor setup. Turbine flow sensors (McMillan Company, FLO Sensor 100) and proportional control valves (Burkert, Germany) were used for on-line measurement and control of the gas flow rate. Gas superficial velocity (V_G) was evaluated considering the free transversal area of the riser. Permeate was collected by means of peristaltic pumps (Watson Marlow 323U), that provided the required TMP. TMP was measured by a pressure sensor (AE Sensors ATM) located in the permeate line. Analogic signals were processed with a Field Point module (National Instruments) connected to a PC running Lab-View 7.1 (National Instruments). Reactors were fed with synthetic wastewater based on a mixture of volatile fatty acids as COD source. The acetate:propionate:butyrate ratio was 2:1:1, expressed as COD. Reactors were operated at a total solids concentration (TSS) of 40 g/L, except when otherwise indicated.

Table 3.1: Equations for steady state determination (Cao and Rhinehart, 1995).

Firs order filter of process variable	$X_{fi} = \lambda_1 X_i + (1-\lambda_1) X_{f\,i-1}$
Estimates of variance	$s_{1\,i}^2 = \frac{2-\lambda_1}{2} \nu_{f\,i}^2$, $\nu_{f\,i}^2 = \lambda_2 (X_i - X_{f\,i-1})^2 + (1-\lambda_2)\nu_{f\,i-1}^2$
	$s_{2i}^2 = \frac{\delta_{f\,i}^2}{2}$, $\delta_{f\,i}^2 = \lambda_3 (X_i - X_{i-1})^2 + (1-\lambda_3)\delta_{f\,i-1}^2$
R statistic	$R_i = \frac{s_{1\,i}^2}{s_{2i}^2} = \frac{(2-\lambda_1)\nu_{f\,i}^2}{\delta_{f\,i}^2}$

X_i represents in this case the TMP.

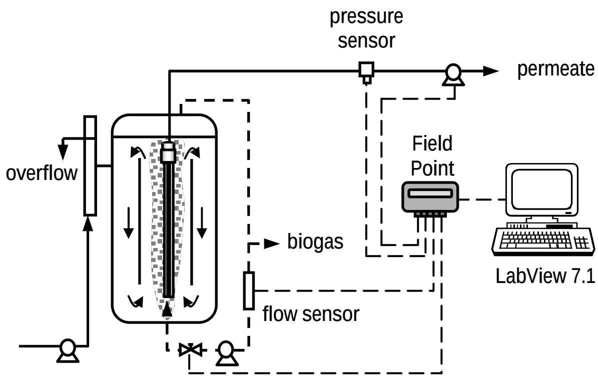


Figure 3.1: Schematic representation of Anaerobic Membrane Bioreactors set-up.

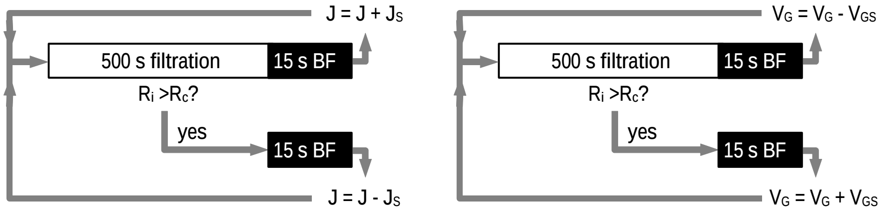
3.2.3. Critical flux determinations

Critical flux was determined applying a flux step method, as already described in Chapter 2. Flux steps were 10 minutes long, and flux increments were 1 $L/m^2{\cdot}h$. One minute of back-flush was included between each cycle. R statistic was calculated during the critical flux measurement in order to establish its ability to reliably detect increases in TMP. The increase in TMP at each step was also tested using an hypothesis test to the rate dTMP/dt, with null hypothesis dTMP/dt = 0 (Montgomery et al., 2001). The significance level was 95%.

3.2.4. Reactors operation

Both reactors were continuously operated in order to test the feasibility of steady state analysis for the control of the flux. The operational strategy consisted of a basic operation cycle of 500 seconds of filtration, followed by 15 seconds of back-flush. During the filtration period, the steady state statistic R was evaluated on-line. First 60 seconds of filtration were not considered in this calculation, to establish a stable TMP. During or after completing each cycle, corrective measurements were performed, depending if during the filtration time the value of R exceeded the critical value (R_C). The type of corrective measurement depended on the variable selected for control. In our case this was either V_G or permeate flux. However, the proposed approach can be used to control any parameter that affects cake layer formation. If the flux is selected as manipulated variable, and R exceeds R_C, the flux should be decreased. On the other hand, if R does not surpass R_C, then the flux is below the critical value and can be increased (Figure 3.2A). Both reactors were operated for 6 days with the describe procedure, with flux as manipulated variable, under different gas flow rates to determine the capability of the proposed approach to control cake formation. The applied flux steps (J_S in Figure 3.2A) were 0.25 L/m^2·h.

It must me noted that in full-scale applications, the effluent flux is not the most proper parameter for managing cake layer formation, since it is imposed by the flow of wastewater to be treated. Therefore, other operational conditions must be selected for controlling cake layer formation, in order to operate the reactor under sub-critical conditions. In large scale submerged MBRs gas sparging is by far more convenient for managing cake layer formation as it directly influences the critical flux. The mesophilic reactor was operated applying the steady state critical flux determination tool, with gas flow rate as manipulated variable (at a fixed flux), according to the scheme in Figure 3.2B. If R exceeds its critical value, then V_G is increased for the next cycle, otherwise it is decreased. V_G steps were 7 m/h (V_{GS} in Figure 3.2B).



(A) Manipulated variable: flux **(B) Manipulated variable: gas flow**

Figure 3.2: Operation strategies for TMP steady state. (A) Flux as manipulated variable, (B) V_G as manipulated variable. J: flux, J_S: flux step, V_G: gas superficial velocity, V_{GS}: gas superficial velocity step.

3.3. Results and discussion

Figures 3.3 and 3.4 present critical flux measurements of thermophilic and mesophilic reactors respectively. Applied flux, TMP and R statistic are presented as a function of time. In both cases, the observed increase in TMP when the critical flux is exceeded triggers a fast increase in R. If a R_C of 2 is considered (Cao and Rhinehart, 1997), critical fluxes of 6 and 17 L/m²·h can be identified for thermophilic and mesophilic reactors, respectively. The same values are obtained when evaluating the critical flux via hypothesis test on dTMP/dt. Our findings show that steady state evaluation is a plain and reliable way to determine TMP increases, and therefore the critical flux.

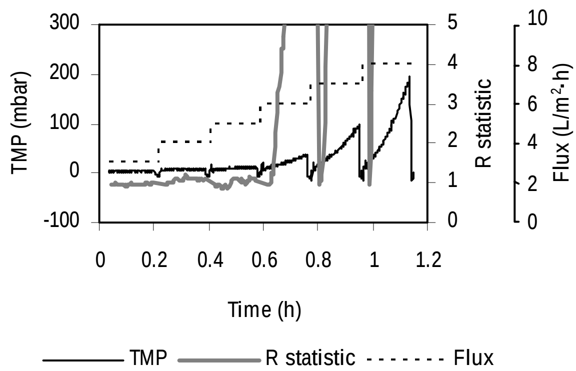


Figure 3.3: Critical flux determination by flux step increase. Flux, TMP and R statistic are presented for the thermophilic reactor. 40 g TSS/L, V_G 70 m/h, λ_1: 0.1, λ_2: 0.05, λ_3: 0.05.

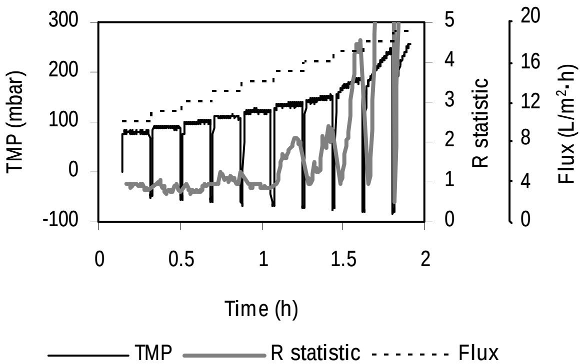


Figure 3.4: Critical flux determination by flux step increase. Flux, TMP and R statistic are presented for the mesophilic reactor, 40 g TSS/L, V_G 60 m/h, λ_1: 0.1, λ_2: 0.05, λ_3: 0.05.

The performance of the control strategy using the permeate flux as the manipulated variable is presented in Figure 3.5, for the thermophilic reactor. TMP and flux evolution over a period of one hour is presented. Figure 3.5 illustrates how flux oscillates around the critical flux: when cake layer formation is detected, an alarm is trigged and consequently, the flux is reduced. If no alarm is trigged during the filtration cycle, the flux is increased. Figure 3.6 presents 6 days of operation of the thermophilic reactor, with the flux as manipulated variable. Figure 3.6A shows the immediate response of the resulting flux on changes in V_G.

The observed pattern can be explained by corrective measures induced by the control strategy in response to changes in V_G, to always keep the maximum flux in absence of significant cake formation, hereby maximizing hydraulic capacity and minimizing cake layer formation. The increase in TMP during the filtration period, that is TMP just before back-flush (TMP PreBF) minus TMP after the back-flush (TMP PostBF), is an appropriate representation of the amount of cake formed during each filtration cycle. The resulting TMP value is presented in Figure 3.6B. Despite the sudden changes in gas flow rate, the TMP increase within the cycles remained below 20 mbar, showing that the cake formation was minimal.

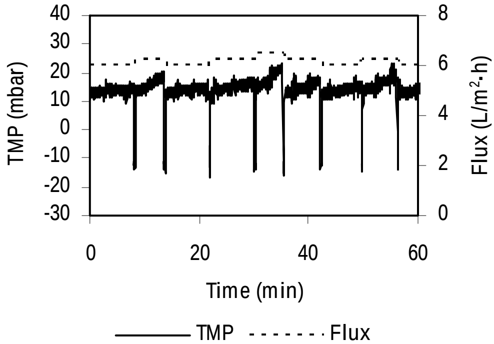


Figure 3.5: Thermophilic AnSMBR operation with TMP steady state control: detection of non-steady state for TMP, flux as manipulated variable. R_C: 2, λ_1: 0.1, λ_2: 0.05, λ_3: 0.05.

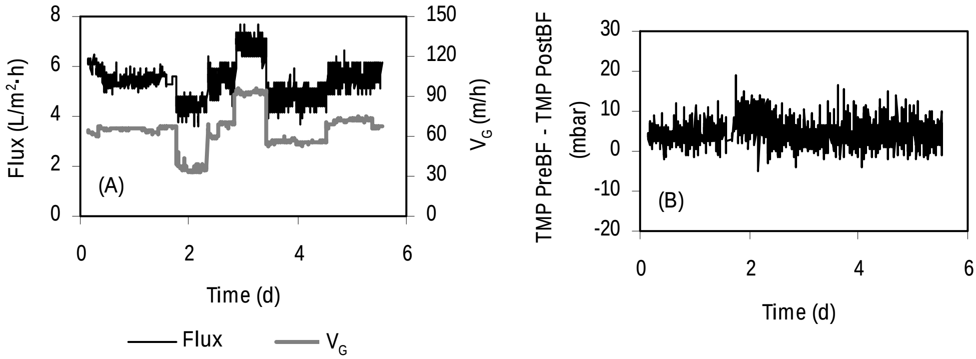


Figure 3.6: Thermophilic AnSMBR operation with TMP steady state control applied to the flux, at different gas flow rates, R_C: 2, λ_1: 0.1, λ_2: 0.05, λ_3: 0.05. (A) Flux and gas superficial velocity, (B) TMP increase during each filtration cycle.

Figure 3.7 presents the operation of the mesophilic reactor, with flux as controlled variable. Again, the control strategy responded rapidly to changes in V_G, keeping the effluent flux in the range of the critical flux. The initial solids concentration was 43 g TSS/L. This concentration was reduce to 37 g TSS/L at the beginning of the third day. On-line flux control readily responded on changes in V_G and also on changes in biomass concentration, two variables that can strongly affect critical flux in AnSMBRs as shown in Chapter 2. The TMP increase during filtration cycles was always below 20 mbar as can be seen in Figure 3.7B.

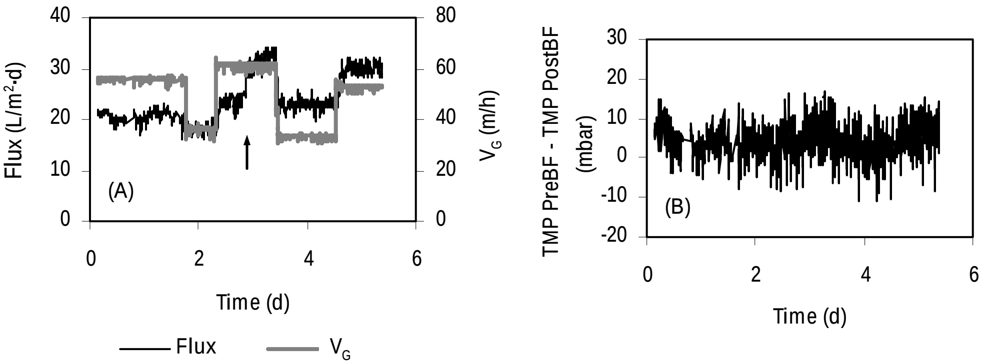


Figure 3.7: Mesophilic AnSMBR operation with TMP steady state control applied to the flux, at different gas flow rates. R_C: 2, λ_1: 0.1, λ_2: 0.05, λ_3: 0.05. (A) Flux and gas superficial velocity. Arrow indicates a decrease of solids concentration from 43 to 37 g TSS/L. (B) TMP increase during each filtration cycle.

The proposed on-line control strategy based on the critical flux shows to be a reliable approach to manage the effluent flux in order to avoid cake formation. However, as mentioned before, effluent flux is usually not available as manipulated variable, since it is fixed by the amount of wastewater to be treated. Figure 3.8 presents the results of applying the proposed strategy using V_G as manipulated variable in the mesophilic reactor, over a period of 60 minutes of operation, with a constant permeate flux of 12 $L/m^2{\cdot}h$. The control strategy acts in a similar way than that shown in Figure 3.5. However, here the resulting flux is constant and V_G is being manipulated in order to avoid cake formation. Again, the increase in pressure triggers an alarm, which stops the filtration cycle and increases the value of V_G. If no alarm is detected, then V_G is reduced. Consequently, V_G oscillates around a value, denominated “critical gas superficial velocity”, which is the value of V_G required to set the critical flux to the flux that is currently being under operation. Figure 3.9 presents 10 days of mesophilic reactor operation, with V_G as manipulated variable. Results show that V_G adequately accommodates to changes in the operational flux, reducing energy requirements to the minimum, while only insignificant cake layer is allowed to develop in the membrane surface. Figure 3.9B presents the increase in TMP during each filtration cycle. Again, values are always below 20 mbar.

An adequate control of the operational conditions directly impacts the economic balance of MBR technology. Treatment systems are usually over-dimensioned in order to accommodate pick loadings. Investment costs of MBR systems are higher than traditional technologies, due to the expenses related with the membranes themselves. Over-dimensioning the membrane requirements can severely reduce the competitiveness of membrane based processes. If MBR systems are designed to be operated with a variable energy input, membrane requirements are smaller, since pick loads can be accommodated manipulating hydrodynamic conditions (Chua et al., 2002). The proposed operation strategy represents a valuable tool in designing such energy efficient MBRs systems. Our control strategy is based on short-term observations of TMP evolution and will mainly respond to cake formation. Wastewater treatment MBRs usually operate under high solids concentration, particularly anaerobic MBRs. Under these conditions, cake formation is likely to be one of the most important reasons for flux reduction or TMP increase.

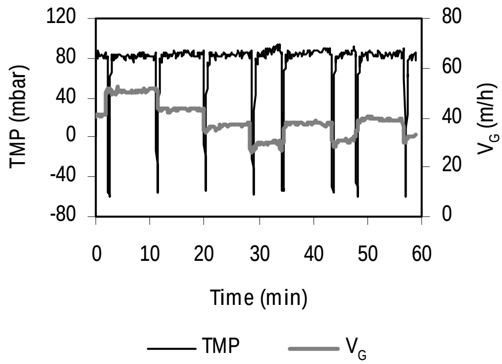


Figure 3.8: Mesophilic AnSMBR operation with TMP steady state control: detection of non-steady state for TMP. Flux: 12 L/m^2·h, V_G as manipulated variable. R_C: 2, λ_1: 0.1, λ_2: 0.05 λ_3: 0.05.

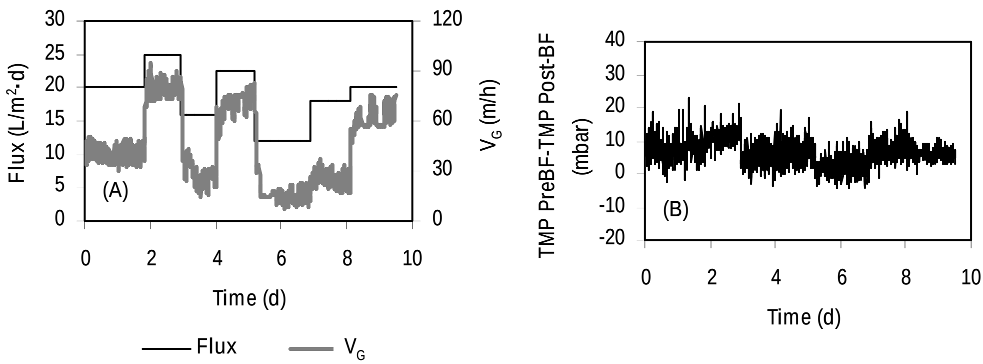


Figure 3.9: Mesophilic AnSMBR operation with TMP steady state control applied to the gas flow, at different values of applied flux. R_C: 2, λ_1: 0.1, λ_2: 0.05 λ_3: 0.05. (A) Flux and V_G, (B) TMP increase during each filtration cycle.

3.4. CONCLUSIONS

A new operational approach for MBR is presented. It is based in an on-line critical flux determination, based on TMP steady state analysis. The novel approach was tested under different operational conditions, for controlling flux or gas superficial velocity in order to minimise cake layer formation and consequently minimize energy consumption. Under all conditions tested, the proposed strategy resulted in a good MBR performance, keeping TMP increase per cycle below 20 mbar. The developed approach represents a valuable tool to the optimal operation of MBR systems.

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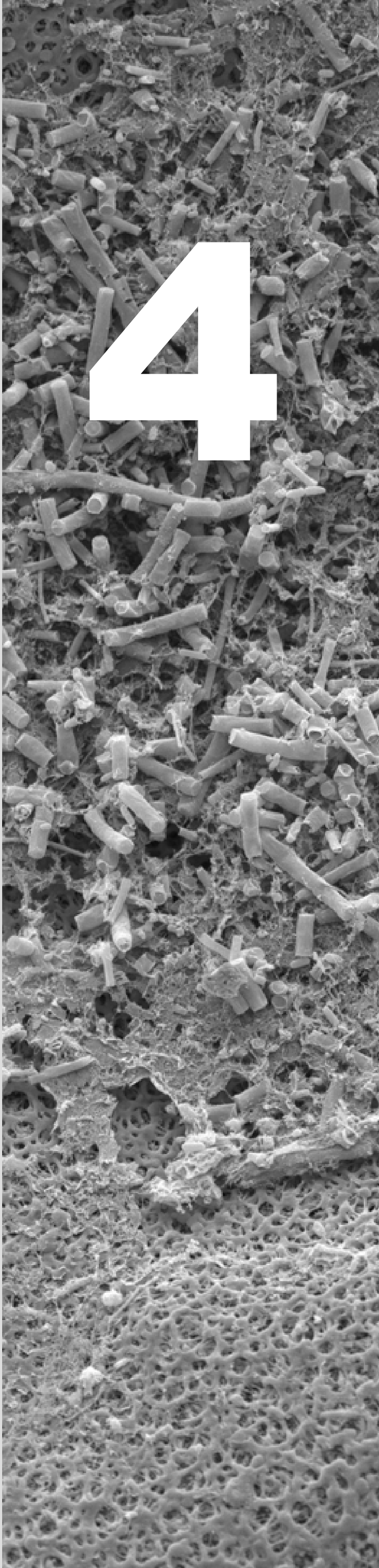

Cake formation and consolidation: Main factors governing the applicable flux in anaerobic submerged membrane bioreactors treating acidified wastewaters

Abstract

A laboratory scale anaerobic submerged membrane bioreactor was operated for over 200 days, with a volatile fatty acids mixture as substrate. Gas sparging was used for mixing and to provide membrane surface shear. Results show that cake formation was entirely governing the applicable flux. Cake formation showed to be mainly reversible on a short term basis, however cake consolidation was observed when a long-term operation was performed at a flux close to the critical flux. Consolidated cake could not be removed by back-flush cycles, and required an external physical cleaning procedure. Surprisingly, low levels of internal pore fouling were observed, significantly decreasing the need for chemical cleaning. The critical flux towards the end of the operation period reached 20 $L/m^2 \cdot h$, at a solids concentration of 40 g/L and a gas superficial velocity of 57 m/h. Further increases in gas superficial velocity were ineffective in achieving a substantially higher critical flux.

4.1. INTRODUCTION

Biomass immobilization and/or retention are key features of most modern biological technologies for wastewater treatment. In anaerobic bioreactors for wastewater treatment biomass retention is of most importance, since it enables the uncoupling of hydraulic and solids retention times, making biomass concentration independent of the low growth rates of methanogenic consortia. Biofilm or granule formation is the most common strategy for biomass retention in anaerobic high-rate reactors for wastewater treatment. During the last 15 years, the use of membrane separation for biomass retention has received increasing interest. Membrane bioreactors (MBR) have the advantage of total biomass retention. They enable the retention of slow growing microorganisms and of those incapable of forming big aggregates.

As already discussed in Chapter 1, most of the reported research on anaerobic MBRs has been conducted with the side-stream configuration. A high cross flow velocity normally involves an important source of energy consumption due to pumping. Furthermore, high shear stress levels can disrupt anaerobic bio-solids and harm the biological activity of anaerobic biomass (Choo and Lee, 1996; Brockmann and Seyfried, 1997). The application of submerged MBRs might overcome the problems frequently observed with the cross flow setup. Low trans-membrane pressures (TMP) and low energy requirements are common characteristics of submerged MBRs (Stephenson et al., 2000). However higher membrane areas are required, in comparison with the side-stream configuration, due to lower surface shear.

In Chapter 2 we already studied the effect of biomass concentration and gas sparging rate over the critical flux, showing that cake layer formation is the limiting step for the applicable flux, when operating a mesophilic anaerobic submerged membrane bioreactor (AnSMBR). Fluxes in the range of 15-20 L/m^2·h were achieved, using gas sparging for mixing and fouling control, at solids concentrations around 35 g/L. However, the study presented in Chapter 2 was based on short-term experiments, where cake formation is more likely to be the phenomena determining the applicable flux. In the current Chapter we present results on the long term operation of a mesophilic AnSMBR system for wastewater treatment. Critical factors for stable long term operation are identified and discussed.

4.2. MATERIALS AND METHODS

4.2.1. Reactor setup and operation

The same mesophilic AnSMBR described in Chapter 2 was used to conduct this study, using also the same anaerobic biomass and the same membrane module. Membrane was chemically cleaned before the operation started. The reactor was fed with a synthetic wastewater based on volatile fatty acids (VFA) as chemical oxygen demand (COD) source. The acetate:propionate:butyrate ratio was 2:1:1, expressed as COD. Inlet COD concentration was set to 10 g COD/L. The reactor was operated with a cycle consisting of 5 minutes of filtration, followed by 30 seconds of back-flush. Back-flush was applied by reversing the flow direction, keeping the flux at the same value than during filtration. Throughout the study, the reactor was operated at a gas superficial velocity in the riser (V_G) in the range 60-65 m/h. AnSMBR was operated at a temperature of 30 °C.

4.2.2. Analyses

Total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to Standard Methods (APHA *et al.*, 1998). Permeate viscosity was determined using a capillary U-tube viscometer (Tamson instruments, The Netherlands). Sludge rheology was measured using a rheometer (CVO, Bohlin instruments, UK). Sludge floc size distribution was measured by laser diffraction analysis (Coulter LS230, Beckman Coulter, USA), and is presented as volume a distribution. Volatile fatty acids were determined in an Hewlett-Packard gas chromatograph (model 5890 series II) with a flame ionization detector (FID), equipped with a column AT Aquawax-DA (Alltech).

The specific methanogenic activity (SMA) was determined in duplicates by pressure increase in experiments performed in 117 mL serum bottles, with 50 mL of media. Measurements were performed at 30 °C. Biomass concentration was 1 g VSS/L. A neutralized VFA mixture of acetate, propionate and butyrate at a COD ratio of 1:1:1, was used as substrate, at an initial concentration of 1.5 g COD/L. Basal medium consisted of (mg/L): NH_4Cl (170), $CaCl_2 \cdot 2H_2O$ (8), KH_2PO_4 (37), $MgSO_4 \cdot 4H2O$ (9), yeast extract (200), $FeCl_3 \cdot 4H2O$ (2), $CoCl_2 \cdot 6H_2O$ (2), $MnCl_2 \cdot 4H_2O$ (0.5), $CuCl_2 \cdot 2H_2O$ (0.03), $ZnCl_2$ (0.05), H_3BO_3 (0.05), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.09), $Na_2SeO_3 \cdot 5H_2O$ (0.10), $NiCl_2 \cdot 6H_2O$ (0.05), EDTA (1), HCl 36% (1 mL/L). The SMA was evaluated as the maximum specific methane production rate.

4.2.3. Apparent membrane resistance and critical flux determinations

Apparent membrane resistance was determined following the procedure already described in Chapter 2. The critical flux was determined applying a flux step method, as also already described in Chapter 2. During critical flux measurements, flux increments of 2 L/m^2·h were applied, including one minute of back-flush between each cycle.

4.2.4. Membrane observation with scanning electron microscope

Membrane samples were taken from the AnSMBR to be observed under the scanning electron microscope (SEM). Samples were collected by cutting small pieces from the end of one of the membrane tubes. Membrane tube was then re-sealed to allow its further use. Samples were fixed with a 2.5% glutaraldehyde solution. Samples were dried in a critical point drier, after being previously de-hydrated, exposing them to increasing concentrations of ethanol solutions. Dried samples were observed in a JEOL 6300F scanning electron microscope.

4.2.5. Physical and chemical membrane cleaning

Two types of membrane cleaning procedures were used to reduce filtration TMP during the operation of the AnSMBR: chemical and physical cleaning. Chemical cleaning was performed according to the membrane supplier recommendations (Triqua, The

Netherlands): 60 minutes acid cleaning with citric acid at pH 3, followed by 60 minutes of oxidative cleaning, with 500 mg/L NaOCl at pH 11. The membrane was chemically cleaned in a separated tank, by submerging it in the cleaning solutions and applying a back-flush flux of 20 $L/m^2 \cdot h$, using the same cleaning solutions. Gas sparging was used to provide mixing. Physical cleaning consisted of the physical removal of the cake layer from the membrane, by flushing the membrane surface with a jet of pressurized water, and gently scouring the membrane surface. Chemical cleaning was performed on days 69 and 173. Physical cleaning was performed on days 123 and 164.

4.3. Results and discussion

Figure 4.1 presents the applied organic loading rate (OLR) and the VFA removal, expressed as COD, during the operation of the AnSMBR. After the start-up was finished (day zero), the loading rate was further increased reaching 32 g COD/L·d on day 40. Between days 60 and 70 the reactor was stopped, and the membrane was extracted from the reactor for chemical cleaning. The reactor was re-started on day 70 at an OLR of 10, to allow re-activation of the biomass. OLR was then further increased, reaching values in the range of 50 to 60 g COD/L·d, towards the end of the operation. Removal rates were extremely high, most of the operation over 98%. Typical permeate VFA concentrations were around 80 mg COD/L. Periodic sludge purges were performed in order to keep TSS concentration at 40 g/L. Mean VSS concentration throughout the operation was 35 g/L, with a standard deviation of 2.7 g/L. If latter VSS concentration is considered, the applied specific loading rates were up to 1.6 g COD/g VSS·d. Working with a similar substrate in a side-stream MBR, Fuchs et al. (2003) reached an organic loading rate of 20 g COD/Ld, at a TSS concentration of 20-25 g/L. This represents less than half the volumetric loading rate obtained in this study. High volumetric and specific loading rates were the result of the development of a high sludge activity. Figure 4.2 presents the evolution of the SMA during the AnSMBR operation. By the end of the operational period, the SMA reached about 2.7 g COD/g SSV·d. This high activity can be explained by the reduction in diffusional restrictions for the substrates, since the sludge inside the reactor mainly consisted of flocs (see Figure 4.3). For the same reason, in anaerobic biofilms and granules usually only the outer layer is active (Alphenaar et al., 1993). The reduction of internal mass transfer limitations in AnSMBRs increases the percentage of active biomass, yielding higher specific activities. This in turn allows higher volumetric conversion rates, provided a high biomass concentration is attained.

Under anaerobic conditions, biofilm formation is not only important with respect to biomass retention, but also because it enhances syntrophic interactions by reducing the transfer distances of intermediary compounds between the different microorganisms (Stams, 1994). Due to unfavourable thermodynamics for the degradation of propionic and butyric acids, a low hydrogen partial pressure is required. This is accomplished in granular biomass due to an efficient interspecies transfer of hydrogen form the hydrogen producing bacteria, to the hydrogen utilizing methanogens. Destruction of granules may then harm interspecies hydrogen transfer due to an increase of the distance between syntrophic bacteria (Schmidt and Ahring, 1996). Figure 4.3 presents the particle size distribution of the sludge from the AnSMBR. Distributions measured at days 17, 140 and 223 are presented.

Average particle size remained within 70 and 90 µm throughout the operation. High reactor performance and sludge activity suggests that even though no granules were present in the MBR, aggregation in small flocs was apparently sufficient to provide suitable conditions for interspecies hydrogen transfer.

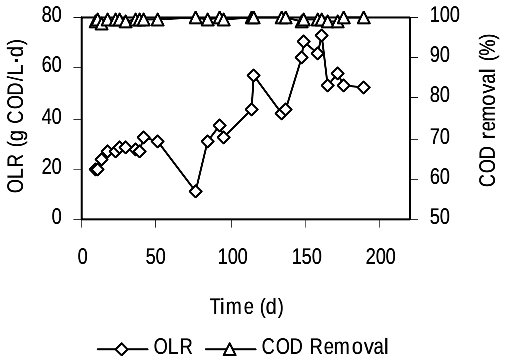

Figure 4.1: Applied OLR and VFA removal (expressed as COD) during the operation of the AnSMBR.

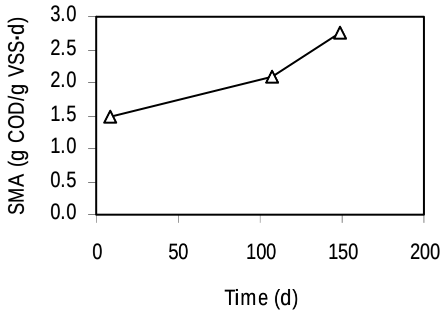

Figure 4.2: SMA of the sludge from the AnSMBR. Standard deviation between the duplicates was below 5 % of the mean.

Figure 4.4 presents the applied permeate flux, and measured TMP during the operation of the AnSMBR. Operational fluxes averaged between 15 and 25 L/m^2·h. Starting from day 100, the reactor was operated with a controlled flux at the range of the critical flux, so without appreciable TMP increase within each operational cycle. The on-line tool based on the TMP evolution described in Chapter 3 was used for this purpose. Unfortunately, the development of a consolidated cake layer hampered the on-line critical flux determination: cake compression during filtration and its relaxation during back-flush cycles induced changes in TMP not related with particle deposition. This resulted in continuous changes in the applied flux, as observed in Figure 4.4.

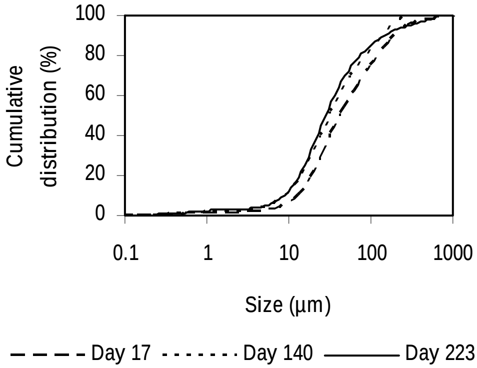

Figure 4.3: Cumulative particle size distribution measured at days 17, 140 and 223 during the operation of the AnSMBR.

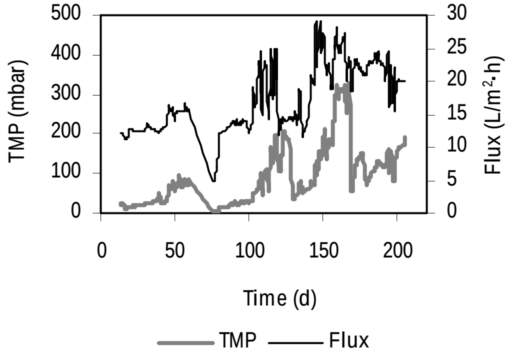

Figure 4.4: Applied permeate flux and measured TMP during the operation of the AnSMBR.

The development of a permanent cake layer over the membrane surface can be clearly observed if filtration resistances are analyzed. Figure 4.5 presents the filtration resistance during the reactor operation, calculated with the TMP and applied flux presented in Figure 4.4. The apparent membrane resistance is presented for comparison. Figure 4.5 shows that the filtration resistance and the apparent membrane resistance are similar throughout the AnSMBR operation. This means that the observed increasing tendency of the filtration resistance during the operation was not related with a reversible, but with an irreversible phenomenon. The term reversible is used here to account for those phenomena that can be reverted by the applied back-flush cycles. If important levels of reversible fouling or reversible cake formation would have occurred during the operation, then filtration resistance should be higher than the apparent membrane resistance, since reversible resistance sums up to the irreversible resistance already considered in the determination of apparent membrane resistance. Figure 4.5 also shows that physical cleaning produced an important decrease in the filtration resistance and in the apparent membrane resistance.

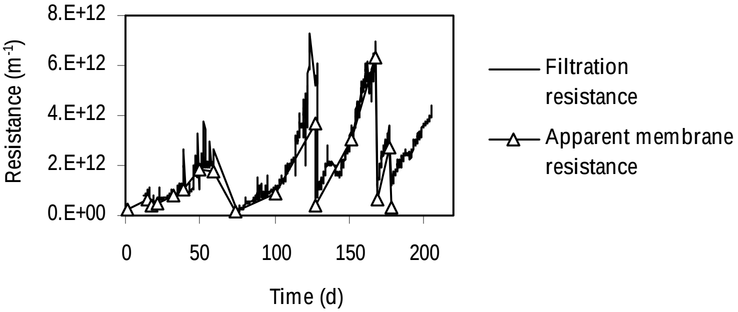

Figure 4.5: Filtration resistance and apparent membrane resistance during the operation of the AnSMBR.

The high extent of physical cleaning efficiency shows that increase in filtration resistance is mainly the result of external cake formation and not internal pore fouling, since the applied physical cleaning is a superficial treatment, and can only remove the material accumulated over the membrane surface. Figure 4.5 also shows a significant reduction in resistance after chemical cleaning procedures, as expected. Table 4.1 presents the four cleaning procedures performed during the operation of the AnSMBR. Apparent membrane resistances before and after the cleaning procedures are presented. The cleaning efficiency is defined as the percentage of reduction of resistance in relation to the new membrane resistance, and it is evaluated as follows:

$$\text{Cleaning Efficiency} = 100\frac{R_{before} - R_{after}}{R_{before} - R_{new}}$$

where R_{before}, R_{after} and R_{new} represent the resistance before the cleaning, after the cleaning and that one of the new membrane, respectively. Table 4.1 shows physical cleanings performed at days 123 and 164 were highly efficient in reducing filtration resistance, reaching cleaning efficiencies close to 90%. First chemical cleaning achieved an almost complete cleaning efficiency, as can be seen in Table 4.1.

Table 4.1: Effect of cleaning procedures on the apparent membrane resistance, during the operation of the AnSMBR.

Time (d)	Type of cleaning	R_{before} (m^{-1})	R_{after} (m^{-1})	Cleaning Efficiency	R_{after}/R_{new}
69	Chemical	$1.7\cdot10^{12}$	$1.8\cdot10^{11}$	99.7%	1.03
123	Physical	$3.7\cdot10^{12}$	$4.1\cdot10^{11}$	88.9%	2.40
164	Physical	$6.3\cdot10^{12}$	$6.6\cdot10^{11}$	89.5%	3.88
173	Chemical	$2.7\cdot10^{12}$	$3.2\cdot10^{11}$	87.9%	1.91

New membrane resistance: $1.70\cdot10^{11}$ (m^{-1})

Figure 4.6 presents SEM pictures of the membrane surface, acquired after and before the chemical cleaning of day 69. Figure 4.6A confirms the high efficiency of chemical cleaning of day 69, since no apparent fouling is visible on the membrane surface. Figure 4.6B shows the cake layer present before the cleaning operation. Chemical cleaning performed on day 173 was not as effective as the one performed on day 69. Chemical cleaning performed during this research was fixed to 2 hours. Probably further time would have been required to achieve a higher restoration of membrane permeability during the second chemical cleaning.

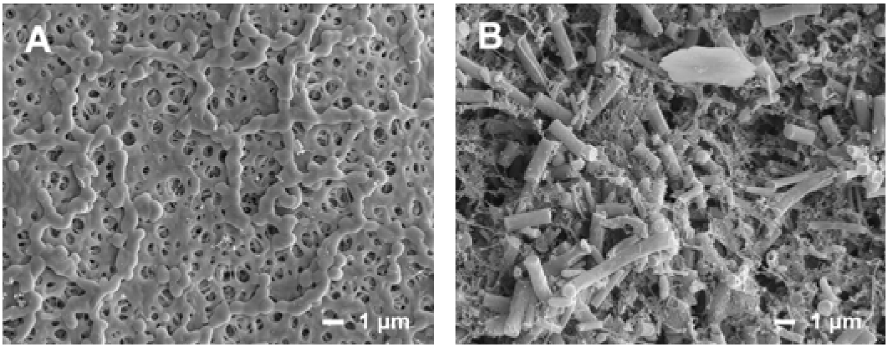

Figure 4.6: SEM images from membrane surface, after (A) and before (B) the chemical cleaning performed on day 69.

The development of a stable cake layer over the membrane surface could be also clearly observed during the measurements of apparent membrane resistance. Figure 4.7 presents the apparent membrane resistance measurements performed after and before the physical cleaning on day 164. TMP values during the filtration and the back-flush periods are presented. After the physical cleaning procedure, TMP during filtration and back-flush are coincident. Filtration resistance through the membrane is then independent of the direction of flow (filtration or back-flush), as expected. However, before physical cleaning there is a remarkable difference between filtration and back-flush TMPs. This difference yielded different resistances: $6.3 \cdot 10^{12}$ m^{-1} for filtration and $2 \cdot 10^{12}$ m^{-1} for back-flush. This behaviour can be explained by the presence of a stable layer over the membrane surface. During filtration this layer compresses, producing a higher resistance. During the back-flush it relaxes, yielding a lower resistance. As mentioned before, the presence of this layer significantly hampered the on-line critical flux determination, since TMP increase during filtration can also occur due to cake layer compression, and not necessarily due to solids deposition.

Critical flux remained fairly constant during the first 100 days of operation, showing a small increase between days 120 and 170, as can be seen in Figure 4.8. Resistance build up, when the flux exceeded the critical value during critical flux measurements, was easily reverted by the imposed back-flush cycles. This indicates that the critical flux is governed by a mainly reversible cake formation. Comparison of Figures 4.4 and 4.8 shows that during part of the operation, the critical flux was indeed exceeded. Working with colloidal silica particles, Chen et al. (1997) observed cake consolidation, resistant to re-dispersion, when operating over critical flux. Although during the first 60 days of operation the applied flux was below the critical value, the formation of a stable cake layer was also observed. Ideally, if operation is maintained below the critical flux, no particle deposition should take place. However, back-transport mechanisms are strongly dependent on particle size (Belfort et al., 1994; Altmann and Ripperger, 1997). This means that in systems with a wide distribution of particle size, like the one studied in this research, an average or apparent critical flux is determined by pressure increase observation. So, even though no appreciable increase in TMP is observed within operational cycles, the critical flux for the smaller fraction of particles has been probably exceeded, and slow deposition takes place. With time, cake develops and consolidates, being resistant to re-dispersion by short back-flush cycles.

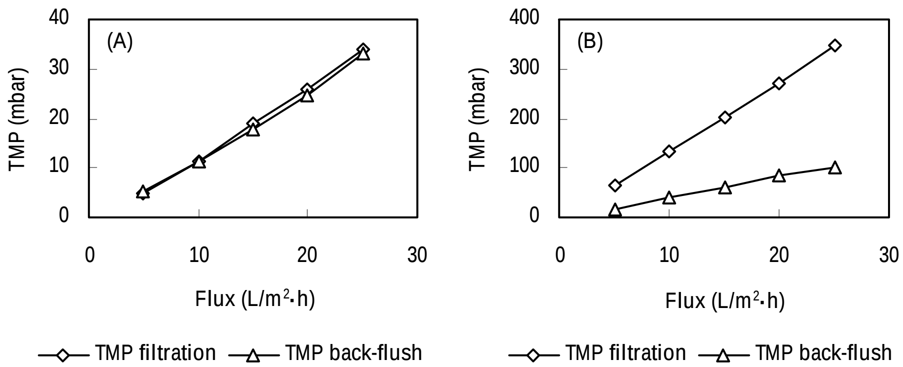

Figure 4.7: Apparent membrane resistance measurements after (A) and before (B) the physical cleaning performed on day 164. TMP during filtration and back-flush periods are presented, against the applied flux.

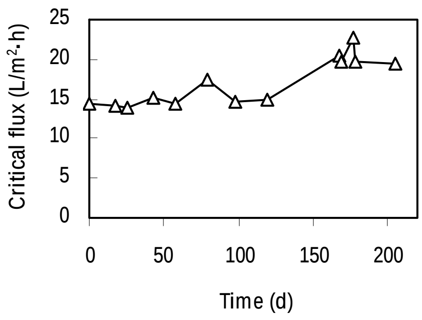

Figure 4.8: Critical flux during the operation of the AnSMBR. Gas superficial velocity in the riser was 57 m/h

The sludge rheological behaviour was assessed at days 45 and 140. The results showed that the sludge rheology was slightly non-Newtonian, showing a behaviour close to a Bingham plastic model (Perry and Green, 1999):

$$\tau = \tau_y + \eta_\infty \dot{\gamma}$$

where τ represents the shear stress, τ_y the shear stress before continuous deformation occurs, η_∞ is the infinite shear viscosity and $\dot{\gamma}$ is the shear rate. On day 45 τ_y and η_∞ were 3.1 Pa and 0.020 Pa·s, respectively. On day 140, values were 1.8 Pa and 0.016 Pa·s, respectively. This means a reduction in apparent viscosity, irrespective of the applied shear stress. The rheological behaviour of the biomass can have a significant effect on the critical flux, since it determines the relation between the shear stress and the shear rate. The decrease in apparent viscosity may have been the cause of the observed change in critical flux between days 120 and 170.

Figure 4.9 presents the effect of V_G on the critical flux, measured at days 43, 114 and 200. V_G during reactor operation was between 60 and 65 m/h. Figure 4.9 shows that a limited increase in critical flux can be achieved by increasing the value of V_G over 50-60 m/h. If the data from day 200 is considered, an increase of 60% in V_G, from 57 to 91 m/h, only produces a 10% increase in critical flux, i.e. from 20 to 22 L/m^2·h. A similar behaviour has been observed in aerobic submerged MBRs: several studies have stated that a critical aeration intensity exists over which no further improve in fouling control can be achieved (Ueda et al., 1997; Liu et al., 2000; Hong et al., 2002).

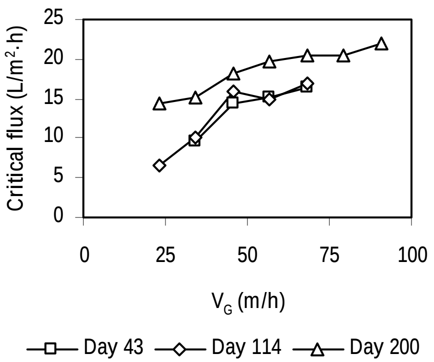

Figure 4.9: Effect of V_G over critical flux, measured at days 43, 114 and 200.

Figure 4.10 presents the TMP increase rates when applying a flux over the critical value, measured during the critical flux determinations performed at day 200. The supra-critical flux is presented as its difference with the critical flux. TMP increase rates rise fast once the critical flux has been exceeded, which further limits applicable fluxes to the range of the critical flux.

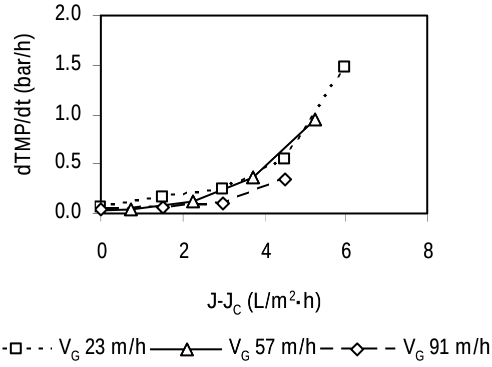

Figure 4.10: TMP increase rate at fluxes over the critical flux, at three different values of V_G. Flux is presented as its difference with critical flux ($J-J_C$).

4.4. Conclusions

During long-term operation of AnSMBR with completely acidified wastewaters, the attained flux is governed by cake formation. Even though cake formation is mostly reversible, cake consolidation can occur during long term operation when the operational flux is in the range of the critical flux. A consolidated cake cannot not be removed by back-flush cycles as applied during our present research, i.e. 30 seconds every 5 minutes. However, a restoration of the membrane permeability is obtained by applying a plain physical cleaning procedure. Interestingly, low levels of internal pore fouling were observed, hardly requiring chemical cleaning. The attained critical flux values were in the range of 20 L/m^2·h, at a TSS concentration of 40 g/L. Increases in gas superficial velocity exceeding a threshold value of 50-60 m/h were ineffective in producing a substantial critical flux increase.

4.5. References

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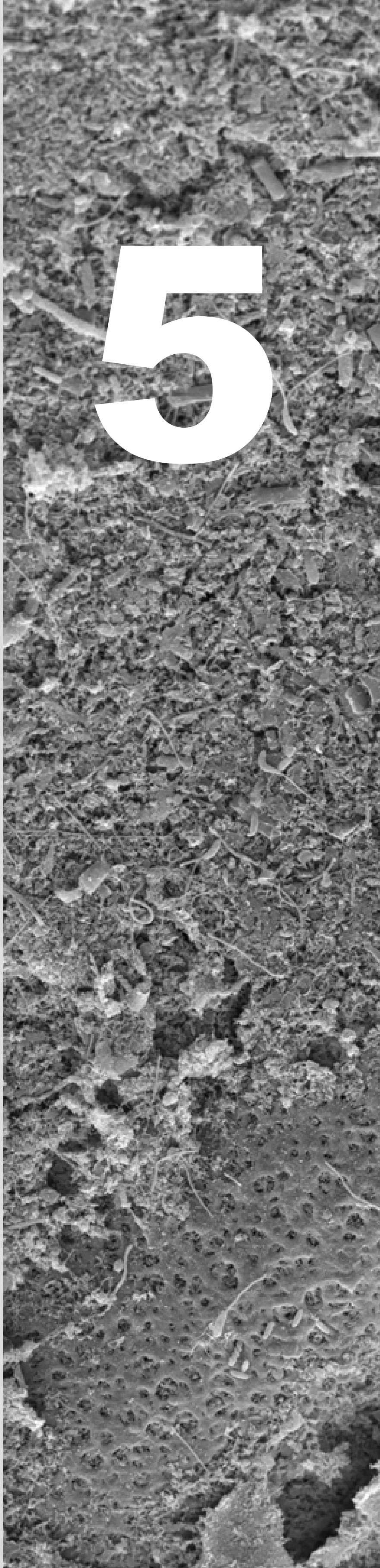

5

Thermophilic treatment of acidified and partially acidified wastewater using an anaerobic submerged MBR: Factors affecting long term operational flux

Abstract

The long term operation of two thermophilic anaerobic submerged membrane bioreactors (AnSMBR) was studied using acidified and partially acidified synthetic wastewaters. In both reactors, cake formation was identified as the key factor governing critical flux. Even though cake formation was observed to be mostly reversible, particle deposition proceeds fast once the critical flux is exceeded. Very little irreversible fouling was observed during long term operation, irrespective of the substrate. Critical flux values at the end of reactors operation were 7 and 3 $L/m^2{\cdot}h$ for the AnSMBRs fed with acidified and partially acidified wastewaters, respectively, at a gas superficial velocity of 70 m/h. Small particle size was identified as the responsible parameter for the low observed flux values. The degree of wastewater acidification significantly affected the physical properties of the sludge, determining the attainable flux. Based on the fluxes observed in this research, the membrane costs would be in the range of 0.33 € per m^3 of treated wastewater. Gas sparging was ineffective in increasing the critical flux values. However, preliminary tests showed that side-stream cross-flow operation may be a feasible alternative to reduce particle deposition.

5.1. INTRODUCTION

Anaerobic treatment is probably the most cost-effective technology for organic matter removal. It is nowadays being successfully applied to a wide range of wastewaters, including both sewage and industrial effluents. The success of anaerobic treatment is attributed to its low operation and maintenance costs and the extreme high loading potentials that are brought about by biomass immobilization. High biomass concentrations, and therefore high sludge ages, can be achieved through biofilm or granule formation.

The potentials of anaerobic technology can be extended if high temperature conditions are applied. Under thermophilic conditions reaction rates are much faster than under mesophilic conditions, indicating higher loading potentials (van Lier, 1995). However, immobilization of thermophilic microorganisms seems to be more problematic than mesophilic microorganisms (van Lier et al., 1997). When biofilm or granule formation is severely affected, membrane assisted separations can be used to achieve sludge retention.

Membrane bioreactors (MBR) represent a breakthrough technology for wastewater treatment. Despite the fact that membranes had been used successfully for many biotechnological industrial applications, high investment and operational costs have hampered their application to wastewater treatment in the past. Intensive research has been conducted in the application of MBR in aerobic wastewater treatment, with interesting results. Many commercial applications are at hand nowadays (Judd, 2006). Additionally, during the last decade, increasing research has been carried out on the application of membrane separation to anaerobic wastewater treatment. This last approach could join advantages of both technologies: a high effluent quality, being a property of MBR technology, with low energy input and high organic loading rates, recognized advantages of anaerobic processes with biomass immobilization.

Recently (Liao et al., 2006) reviewed the application of anaerobic membrane bioreactors, showing that limited number of studies have been done with vacuum driven submerged membrane technology. Also, few studies have been made at thermophilic conditions, where membrane retention can significantly improve treatment performance due to the biomass retention difficulties already mentioned. Submerged membrane technology involves lower energy requirements than side-stream configuration, however, lower applied surface shear usually involves higher membrane requirements.

The present research studies the long term operation of anaerobic submerged membrane bioreactors (AnSMBR) treating acidified and partially acidified wastewaters, under thermophilic conditions. Potentials and limitations for applying thermophilic AnSMBRs are discussed. In order to evaluate the effect of surface shear increase on the attainable flux , complementary operational strategies were researched. The latter include gas sparging under slug flow regime, and high liquid cross-flow velocities in external membranes.

5.2. MATERIALS AND METHODS

5.2.1. Reactors setup and operation

Two identical AnSMBR with a useful volume of 3.7 L were used to conduct this study. Reactors were fitted with tubular polysulphone microfiltration membranes, with a nominal pore size of 0.2 µm (Triqua, The Netherlands). AnSMBRs were operated as gas-lift reactors, with the membrane modules placed inside the riser. A description of the reactors set-up can be found in Chapter 2. Gas superficial velocities (V_G) have been evaluated using the free transversal area of the riser. Both reactors were fed with synthetic wastewaters. The first reactor was fed with a mixture of volatile fatty acids (VFA), with an acetate:propionate:butyrate ratio of 1:1:1, expressed as chemical oxygen demand (COD). This reactor will be referred to as VFA-SMBR. Second reactor was fed with a solution containing glucose and the same VFA mixture used for the first reactor. Glucose represented 50% of the total COD. This reactor will be referred to as glucose/VFA-SMBR. The VFA-SMBR was inoculated with the same thermophilic biomass used for the experiments described in Chapter 2. Glucose/VFA-SMBR was inoculated using sludge coming from the VFA-SMBR, some weeks later. Inlet COD concentration was set to 10 g COD/L. Starting on day 190, the VFA-SMBR was fed with a concentrated VFA solution of 100 g COD/L, which was diluted in-line with tap water. The amount of dilution water was determined by the operational flux, in order to keep the reactor liquid level constant. This allowed the increase of the applied loading rate, independently of the applied flux, by increasing the effective inlet COD concentration. Both reactors were operated with a cycle consisting of a filtration period, followed by a 30 seconds back-flush. Back-flush was applied by reversing the flow direction, keeping the flux at the same value than during filtration. The initial filtration time was 10 minutes, value that was reduced to 5 minutes on days 39 and 23 for the VFA-SMBR and glucose/VFA-SMBR respectively. This reduction was needed due to the rapid trans-membrane pressure (TMP) increase. Reactors were operated at a V_G in the range 70-75 m/h, and at a temperature of 55 °C.

Membranes physical and chemical cleaning procedures were performed as described in Chapter 4.

5.2.2. Side-stream configuration experiments

In order to determine the potential benefits of a side-stream configuration, several critical flux measurements were performed under two alternative set-ups: using gas slug-flow regime and using high liquid cross-flow. Experiments were performed using the VFA-SMBR, or sludge taken from this reactor. In both cases an external membrane module fitted with a single tubular inside/out membrane (permeate flows from the inside to the outside of the membrane tube) was used. Tubular membrane length was 35 cm. The required TMP was provided by applying vacuum to the permeate side of the membrane, by means of a peristaltic pump (Watson Marlow 323U, UK). TMP was measured by a pressure sensor (AE Sensors ATM, The Netherlands) located in the permeate line. Each critical flux determination made under high liquid cross-flow was performed with a fresh sample of sludge from the VFA-SMBR, in order to ensure reproducible conditions. To ensure sludge availability for all determinations, including also preliminary tests, critical flux measurements were done at a lower total suspended solids (TSS) concentration than that of reactor operation, i.e. 30 g/L. Critical flux measurements performed under gas slug flow regime were performed at the same concentration. Critical flux determinations with the submerged configuration at 30 g TSS/L were also performed, as baseline for the evaluation of the side-stream configurations. Figure 5.1 presents a schematic representation of the setups used for the slug-flow and high cross-flow critical flux determinations. All measurements were performed once the operation of the VFA-SMBR was finished. All critical flux determinations were performed at a temperature of 55 °C.

During the first set of experiments, the potential benefit of slug flow regime inside tubular membranes was studied. For that purpose the external membrane module was connected to the VFA-SMBR as shown in Figure 5.1. Biogas was injected in the bottom of the module to generate gas slugs inside the membrane. Liquid recirculation between the reactor and the module was only brought about by the resulting gas lift effect. In order to evaluate the filtration performance, the critical flux was measured under different values of V_G. Two membrane types were tested: a ceramic microfiltration membrane, with 0.2 µm pore size and 6 mm internal diameter (Atech Innovations, Germany); and a polymeric ultrafiltration membrane, 30 nm pore size, 8 mm internal diameter (Norit, The Netherlands).

During cross-flow experiments, a peristaltic recirculation pump (Masterflex I/P, USA) was used to circulate the sludge through the membrane module (Figure 5.1). The membrane module was fitted with a ceramic membrane with the same characteristics as that employed for the slug-flow experiments. Sludge was circulated within the system at the cross-flow velocity of interest for 2 hours before each critical flux analysis was performed. Measurements were done at 1 and 2 m/s of liquid cross-flow velocity (V_L). Measurements with nitrogen gas injection were also performed, applying a V_G that equals about 10% of the liquid superficial velocity.

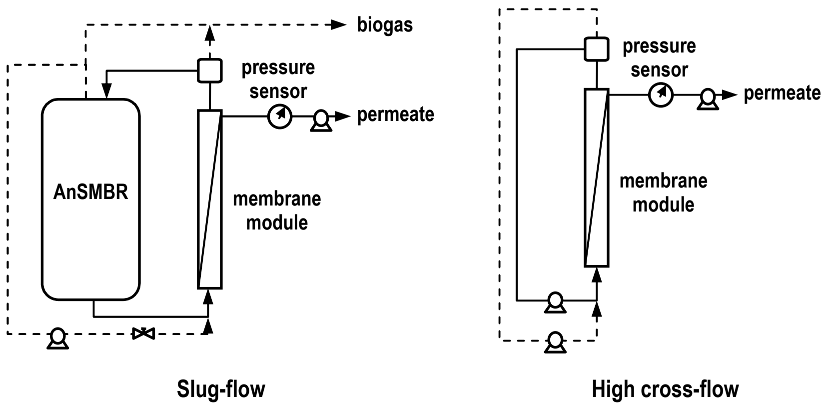

Figure 5.1. Schematic representation of the setups used for the side-stream configuration measurements. Doted lines indicate gas flows.

5.2.3. Apparent membrane resistance and critical flux determinations

Apparent membrane resistance was determined following the procedure already described in Chapter 2. The critical flux was determined applying a flux step method, as also already described in Chapter 2. During critical flux measurements, different flux increments in the range 1-3 $L/m^2 \cdot h$ were applied, depending on the expected value of the critical flux.

5.2.4. *Specific cake resistance*

Specific cake resistance of sludge samples was measured in an unstirred batch filtration unit. A single membrane tube of 55 mm long and 9 mm diameter, with a useful filtration area of 0.00156 m^2, was used for this purpose. Membrane was placed in a 0.12 L useful volume cylindrical glass module that contained the sludge. Measurements were performed at 55 °C. The membranes used for cake resistance determination had the same characteristics as those used for the operation of the reactors. Filtration was performed at constant flux of 10 $L/m^2 \cdot h$, by means of a peristaltic pump that collected the permeate from the membrane lumen. TMP was measured by a pressure sensor located in the permeate line. To avoid sludge settling, sludge circulation was performed, applying a liquid superficial velocity of $8 \cdot 10^{-4}$ m/s, a value that is considered small enough to produce insignificant shear stress over the membrane surface. Measurements where performed in duplicates. During a filtration process, the flux is related with cake and membrane resistance through the resistance in series model:

$$J = \frac{1}{A}\frac{dV}{dt} = \frac{TMP}{\eta}\frac{1}{R_M + R_C} \qquad (1)$$

where J represents the flux, A the membrane area, V the permeate volume, t the time, η the permeate viscosity, R_M the apparent membrane resistance and R_C the cake resistance. In a dead end filtration, cake resistance is related to the specific cake resistance (α) through the amount of deposited particles (Perry and Green, 1999):

$$R_C = \frac{V}{A}\alpha \cdot C \qquad (2)$$

where C represents the solids concentration. If R_C from equation 2 is substituted in equation 1, and a constant flux is assumed, we obtain:

$$TMP = \frac{\eta \cdot \alpha \cdot C \cdot J}{A} V + \eta \cdot R_M \cdot J \qquad (3)$$

The specific cake resistance is then determined through the evaluation of the slope of a plot of TMP against permeate volume.

5.2.5. *Analyses*

TSS and volatile suspended solids (VSS) were determined according to Standard Methods (APHA et al., 1998). COD was determined using Lange COD cuvette tests (LCK 514, Hach Lange, Germany). Permeate viscosity was determined using a Capillary U-Tube Viscometer (Tamson instruments, The Netherlands). Sludge rheology was measured using a rheometer (CVO, Bohlin instruments, UK). Sludge floc size distribution was measured by laser diffraction analysis (Coulter LS230, Beckman Coulter, USA), and is presented as a volume distribution. Volatile fatty acids were determined in a gas chromatograph (Hewlett-Packard model 5890 series II) with a flame ionization detector (FID).

The specific methanogenic activity (SMA) was determined as described in Chapter 4, at a temperature of 55 °C. A neutralized VFA mixture of acetate, propionate and butyrate at a COD ratio of 1:1:1, was used as substrate, at an initial concentration of 1.5 g COD/L. Specific acidogenic activity was determined as the rate of glucose consumption in experiments performed in 117 mL serum bottles with 50 mL of liquid volume. Glucose depletion was determined measuring reduction rate of total carbohydrates in the liquid phase, using a modified anthrone method (Raunkjaer et al., 1994).

5.2.6. Membrane observation with scanning electron microscope

Membrane samples were taken from the VFA-SMBR to be observed under the scanning electron microscope (SEM). Samples were fixed, dried and observed as described in Chapter 4.

5.3. RESULTS AND DISCUSSION

5.3.1. AnSMBRs operation

The VFA-SMBR and the glucose/VFA-SMBR were continuously operated for 300 and 180 days, respectively. The biomass concentration in the reactors was kept at around 35 g TSS/L (27 g VSS/L) and 40 g TSS/L (34 g VSS/L), for the VFA-SMBR and the glucose-VFA-SMBR, respectively. When necessary, sludge wastes were performed in order to keep biomass concentration in these ranges. Figure 5.2 presents the organic loading rate (OLR) and COD or VFA removal during both reactors operation. During the first 60 days of the VFA-SMBR operation, the OLR was around 30 g COD/L·d. From day 70 till 190, OLR had to be reduced to 12-16 g COD/L·d, due to a reduction in operational flux. From day 190 onwards, the increase in inlet COD concentration enabled the increase of the OLR, up to 40 g COD/L·d. VFA removal was high most of the operation, usually over 98%. A decrease in VFA removal can be observed on days 206 and 245, caused by failures of the control equipment which led to involuntary sludge washout. Typical effluent VFA concentrations were around 150-200 mg COD/L. Applied OLR in the glucose/VFA-SMBR was in the range 10-20 g COD/L·d, and was mainly limited by the operational flux. COD removal was over 98% most of the operation.

Figure 5.3 presents the evolution of the SMA of the sludge from both reactors. The sludge from the VFA-SMBR showed a fast increase in SMA during the first few days of operation. SMA reached 2.5 g COD/g VSS·d, and then slightly decreased to 2 g COD/g VSS·d, towards the end of the operation. Low organic loading rates applied during an important part of the operation produced low biomass growth, meanwhile high sludge concentration resulted in important levels of biomass decay. Dead bacteria cannot leave the reactor, contributing to the VSS concentration. The SMA from the glucose/VFA-SMBR showed a continuous decrease from slightly over 2.5 to 1 g COD/g VSS·d. The latter reduction is most likely explained by the low applied loading rates, and also by the dilution of methanogenic and acetogenic microorganisms by the growth of an important proportion of acidogenic bacteria.

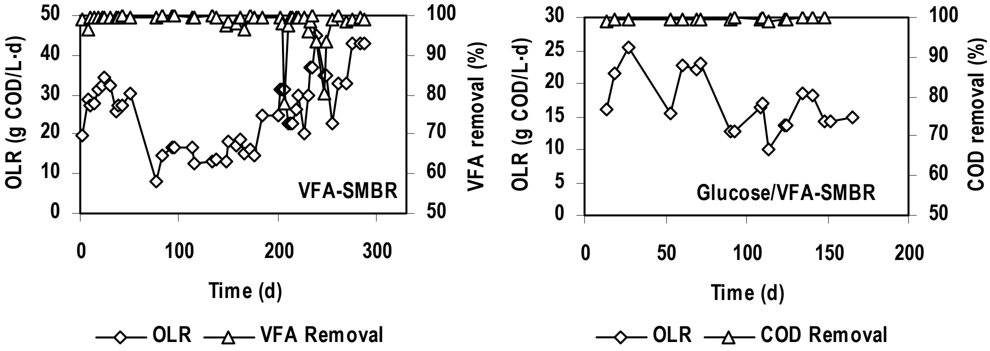

Figure 5.2. OLR and VFA removal during the operation of the VFA-SMBR, and OLR and COD removal during the operation of the glucose/VFA-SMBR.

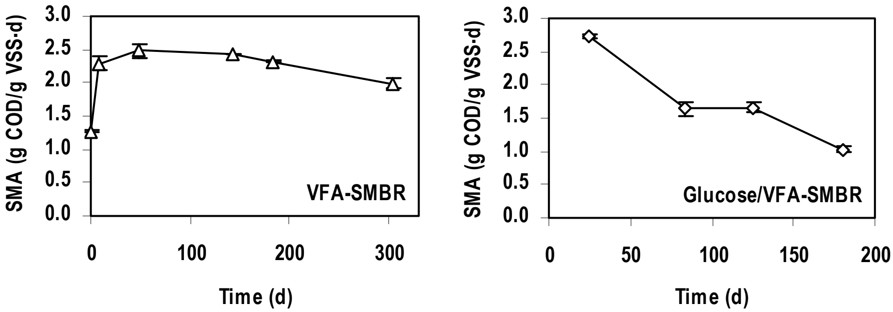

Figure 5.3. Evolution of the SMA during the operation of the VFA-SMBR and glucose/VFA-SMBR. Error bars represent the standard deviation between duplicates.

Figure 5.4 presents the filtration resistance, the applied flux and the apparent membrane resistance during the operation of both thermophilic AnSMBRs. Filtration resistance was evaluated with the measured TMP, applied flux and the permeate viscosity at 55 °C, which was equal to that of clean water. Results are presented as filtration resistance to facilitate comparison and analysis. Initial fluxes for the VFA-SMBR were in the range of 15 $L/m^2{\cdot}h$. However, shortly after the operation started, a continuous TMP increase was observed, resulting from an important rise in resistance. The latter forced a reduction in flux, as can be seen in Figure 5.4. Cake formation was identified as the reason for this resistance increase, since it was almost completely reversible by back-flush cycles. Apparent membrane resistance remained low, showing that little irreversible fouling occurred. Even though build-up resistance during each filtration cycle could be reverted easily by back-flush cycles, particle deposition over the membrane surface proceeded fast. Critical flux determination performed at day 60 showed that at a flux of only 3 $L/m^2{\cdot}h$ over the critical value, the TMP increase rate during filtration reached 1 bar/h. Results clearly demonstrate that, even when particle deposition is mainly reversible, the resulting flux is still restricted to the range of the critical flux due to rapid TMP increase.

The VFA-SMBR was stopped between days 60 and 75 for external chemical cleaning of the membrane. The reactor was re-started at a low flux, and from day 95 onwards the on-line TMP evaluation tool described in Chapter 3 was used to keep the applied flux in the range of the critical flux. The resulting flux remained around 6-7 $L/m^2 \cdot h$, which agreed well with the critical flux measured by the flux step method, presented in Figure 5.5. The latter shows a fast decrease in critical flux during the first 60 days from 20 to 6-7 $L/m^2 \cdot h$; a value that remained more or less constant throughout the entire operational period. Between days 180 and 200, the flux was fixed at 8 $L/m^2 \cdot h$, so only 2 $L/m^2 \cdot h$ over the critical flux. Despite this small increase in flux, an important increase in resistance was observed (see Figure 5.4). If the filtration resistance during the operation over the critical flux is compared with the apparent membrane resistance, it is clear that the apparent membrane resistance only accounts for less than 15% of the filtration resistance, being the rest the result of mainly reversible particle deposition. From day 200 until the end of the operation, VFA-SMBR was operated again with the above-mentioned on-line flux control. Flux returned again to the values already shown before day 180, accordingly with the measured critical flux.

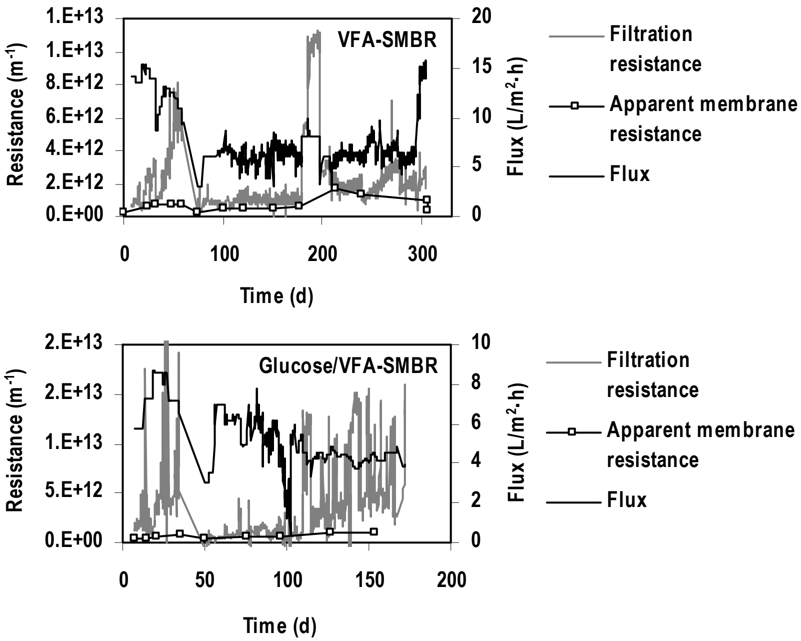

Figure 5.4. Applied flux, filtration resistance and apparent membrane resistance during the operation of the thermophilic AnSMBRs.

Cake formation was also the main limiting factor for the operation of the glucose/VFA-SMBR. During the first 35 days of operation heavy cake formation was observed, which is reflected in the increasing resistances measured during that period (Figure 5.4). As was the case of the VFA-SMBR, this cake formation was almost completely reversible by the application of back-flush cycles. The reactor was stopped between days 35 and 50, and the membrane was chemically cleaned. However, cleaning of the membrane did not improve the MBR operation, and the flux had to be gradually decreased between days 50 and 103 to control the TMP. From day 104 onwards the flux was set to 4-4.5 L/m^2·h, a value that was over the critical flux, as can be seen in Figure 5.5. High filtration resistances resulted from this flux setting, even though the apparent membrane resistance remained low (Figure 5.4). This, again, indicates that reversible cake formation represented the limiting factor for reactor operation, as was also the case for the VFA-SMBR.

Values of apparent membrane resistance from both reactors revealed low levels of irreversible fouling even though MBRs were operated for long periods without chemical cleaning: 230 days in the case of the VFA-SMBR and 125 days in the case of the glucose/VFA-SMBR. Figure 5.5 shows that apparent membrane resistance in the VFA-SMBR remained constant while the reactor was operated in the range of the critical flux, i.e. between days 95 and 180. When the flux was increased over the critical value (from day 180 to 200), an increase in apparent membrane resistance was observed. However, once the flux was decreased, the resistance also decreased, suggesting that cake build up and consolidation may have been the cause of apparent membrane resistance increase during operation over the critical flux. Once the flux was set again to the critical value on day 200, no more particle deposition took place anymore, and part of the previously formed cake detached. Physical cleaning performed at the end of the operation confirms this hypothesis, since it was very effective in restoring membrane permeability, as can be seen in Figure 5.5A.

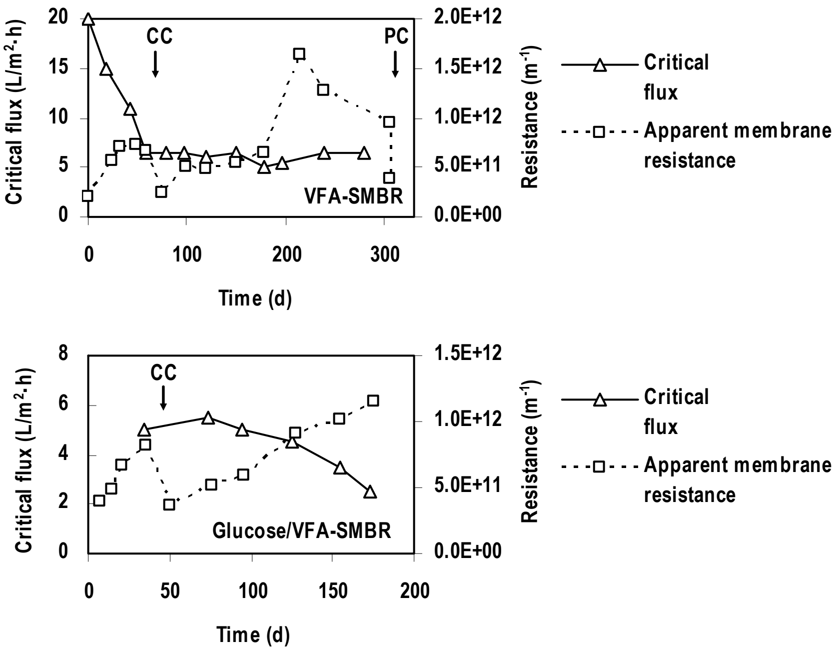

Figure 5.5. Critical flux and apparent membrane resistance during the operation of the thermophilic AnSMBRs. CC: chemical cleaning, PC: physical cleaning. V_G during critical flux measurement was 70 m/h.

The observed reduction of critical flux during the operation of the VFA-SMBR, the high fouling rates over the critical flux and the differences between the reactors are most likely related with different properties of the sludge. Differences observed between filtration resistance and apparent membrane resistance indicate that the critical flux is limited by particle deposition over the membrane surface. If this hypothesis is true, then the membrane itself should not play an important role in the determination of critical flux: once the membrane surface is covered by sludge, it will stop playing a role in the determination of particle deposition. In order to test this, the VFA-SMBR membrane was temporarily replaced by a new one on day 50. The new membrane showed the same tendency for cake formation as the old one. Moreover, the membrane chemical cleaning procedure produced no effect on the filtration behaviour in both reactors. In addition, on day 275, the VFA-SMBR membrane was again temporarily replaced by the membrane being used to operate the mesophilic AnSMBR described in Chapter 4. Several critical flux measurements were performed with both membranes. Interestingly, the critical flux values coincided, even though the membranes had a different operational history. These results give further proof that the reduction of critical flux experimented by the VFA-SMBR is not related with changes in membrane properties due to fouling, but with the properties of the sludge itself.

One of the most important factors affecting particle deposition is particle size, since it can strongly determine the magnitude of back-transport mechanisms (Belfort et al., 1994; Altmann and Ripperger, 1997). Figure 5.6 shows a progressive decrease in particle size during the VFA-SMBR operation. The decrease in critical flux was observed during the first part of reactor operation, when changes in particle size seemed only moderate. However, research done with bidispersed and polydispersed suspensions found that the smallest particle in the suspension can determine the filtration rate (Kim et al., 2002; Kromkamp et al., 2002). Since smaller particles experience a lower back-transport, they show a higher tendency to deposit on the membrane surface. Figure 5.7 presents a SEM picture of the membrane surface, acquired on day 60. A cake layer can be observed which is composed by extremely small particles. Indeed, almost no cells can be observed on the membrane surface. This is probably the result of cell decay or mesophilic cell fragments still remaining from the inoculum. It has to be noticed that thermophilic microorganisms presents much higher decay rates than mesophilic microorganisms (Zeikus, 1979; Speece, 1996).

Figure 5.8 presents SEM images from the membrane surface of the VFA-SMBR, acquired at days 65 (after chemical cleaning) and 305 (before and after physical cleaning). Figure 5.8A shows that chemical cleaning was not 100% effective in removing foulants from the membrane, since some small particles still remain on membrane surface. Indeed, membrane resistance after the cleaning procedure was 18% higher than the resistance of the new membrane. At day 305, the membrane surface is almost completely covered by a cake layer, consisting of cells, colloids and polymers (Figure 5.8B). Mechanical cleaning procedure removed most of the deposited material, as can be seen in Figure 5.8C. The figure also shows that physical cleaning only removed material deposited over the membrane surface, as expected. Internal pore fouling can be appreciated as partially clogged pores. It is also possible that the procedure of physical cleaning had pushed some deposited material inside the pores. Anyway, the removal of the deposited layer reduced membrane resistance from $9.6 \cdot 10^{11}$ to $3.9 \cdot 10^{11}$ m^{-1}. Results indicate that the cake layer observed in Figure 5.8B was the main responsible for the increase in apparent membrane resistance observed especially after the VFA-SMBR operation at a flux over the critical flux (between days 180 and 200).

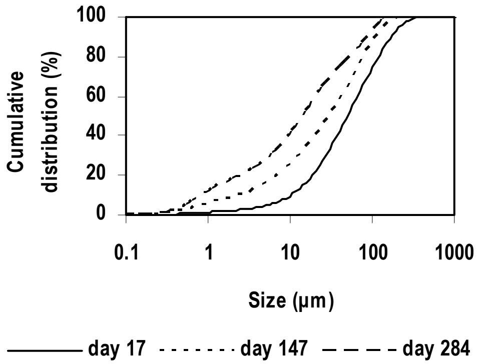

Figure 5.6. Cumulative particle size distribution of the sludge developed in the VFA-SMBR.

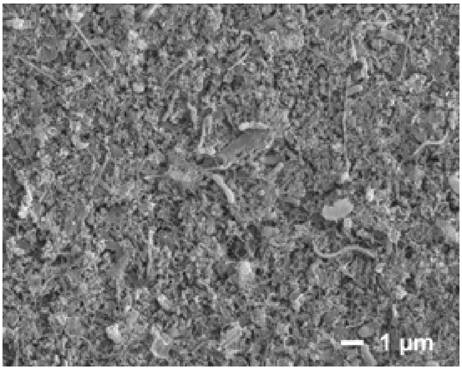

Figure 5.7: SEM picture of the cake layer formed over the membrane of the VFA-SMBR. Image acquired on day 60.

Membrane resistance from the glucose/VFA-SMBR showed an increasing tendency as depicted in Figure 5.5B. However, apparent membrane resistance remained low, below $1.2 \cdot 10^{12}$ m^{-1}. Final membrane resistance for VFA-SMBR (before physical cleaning procedure) was similar, close to $1 \cdot 10^{12}$ m^{-1}. A resistance of $1 \cdot 10^{12}$ m^{-1} means that a driving pressure of only 0.014 bar is required per each 10 $L/m^2 \cdot h$ of flux, at 55 °C. The formation of a cake layer over the membrane that acted as a secondary dynamic membrane may be partly responsible for the low levels of internal fouling observed during this study. This secondary membrane may have "protected" the real membrane, preventing pore blocking and other mechanisms of irreversible fouling.

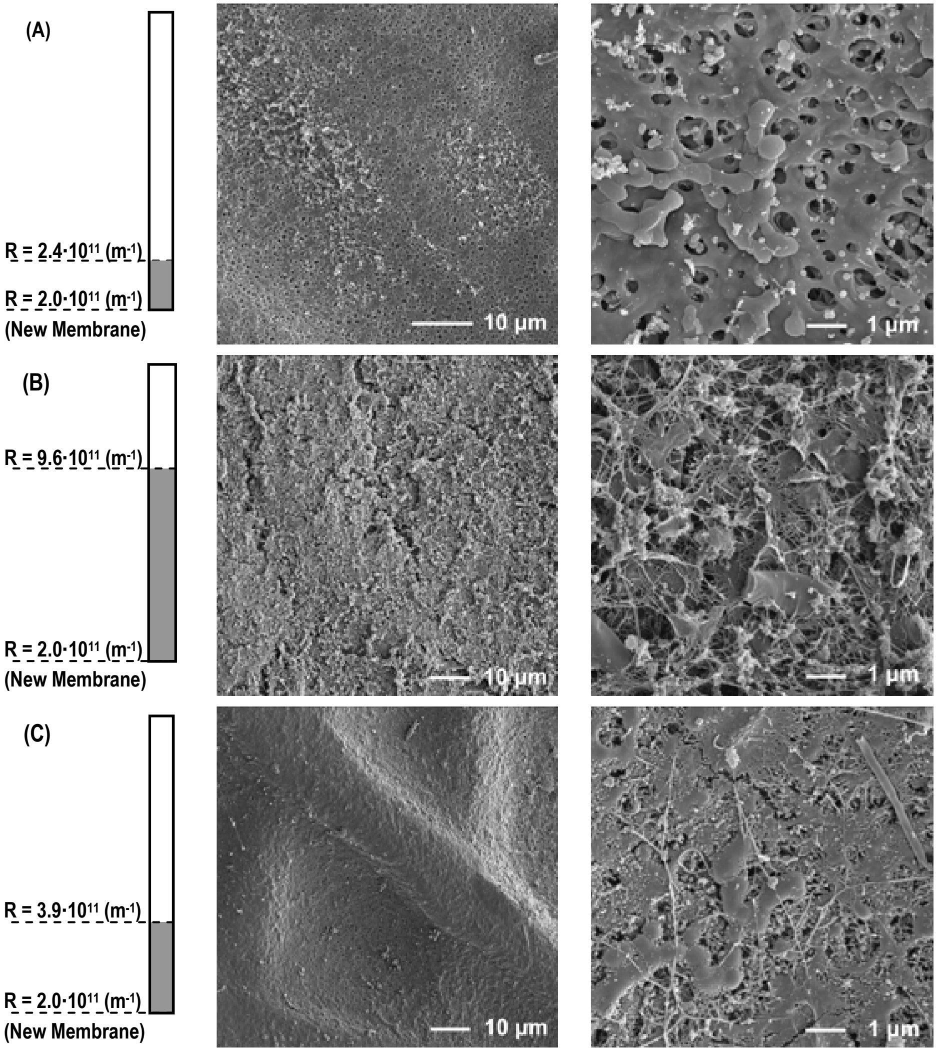

Figure 5.8. SEM pictures of the membrane from the VFA-SMBR: (A) day 65 (chemically clean membrane), (B) day 300, (C) day 300 after physical cleaning. Membrane resistances in each case are presented in the scales on the left, together with the resistance of the new membrane.

Figure 5.9 presents the effect of V_G on the critical flux, measured at the end of the reactors operation. In both cases, increases in V_G only produced small increments in the critical flux. Critical flux values remained below 8 and 4 L/m^2·h for the VFA-SMBR and glucose/VFA-SMBR, respectively, even though a wide range of V_G was tested. Figure 5.10 presents the TMP increase rates over time, when critical flux was exceeded. Presented values were measured at the end of reactors operation. To facilitate comparison, results are presented as a function of the difference between the flux and the critical flux (J-J_C). On both reactors, changes in gas flow rate do not seem to affect the TMP increase rates. However, it has to be considered that since critical flux slightly changed with V_G, the different rates presented in Figure 5.10 were measured at different absolute values of flux. The latter means different convective flow of particles towards the membrane. TMP increase rates observed in the glucose/VFA-SMBR showed to be close to four times higher than those in the VFA-SMBR. In turn, rates in the VFA-SMBR were slightly higher than those observed in the mesophilic AnSMBR described in Chapter 4. However, the mesophilic AnSMBR was operated at fluxes 3 times higher than the thermophilic VFA-SMBR, indicating a much higher convective particle flow towards the membrane surface than under the high temperature conditions.

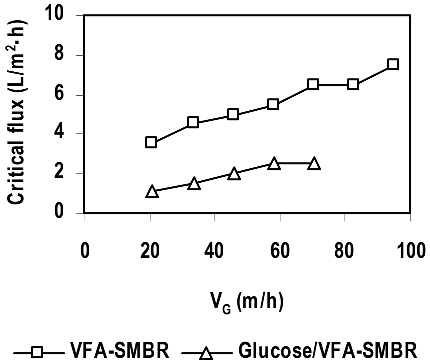

Figure 5.9. Effect of V_G on the critical flux, measured at the end of reactors operation.

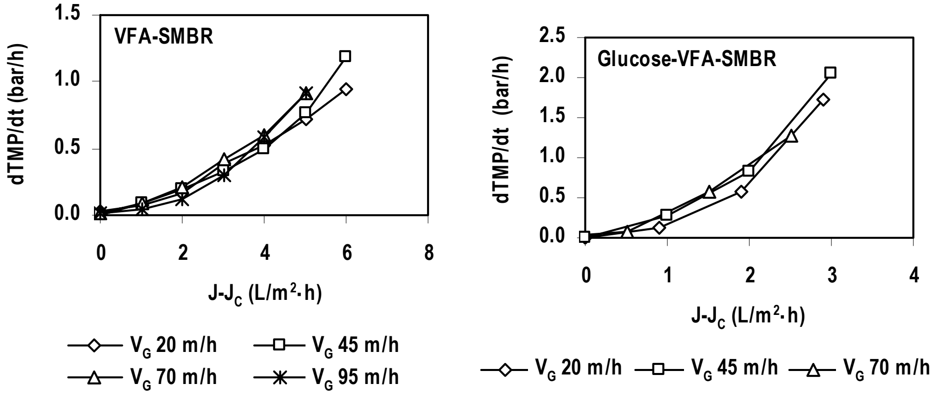

Figure 5.10. TMP increase rates at the end of reactors operation, at different values of V_G.

Both reactors showed very different rheological behaviours, as can be seen in Figure 5.11. Sludge from the VFA-SMBR showed a behaviour very close to that of a Newtonian fluid, with a viscosity of 0.013 Pa·s, at 55 °C. The glucose/VFA-SMBR showed a behaviour close to a Bingham plastic fluid, which is commonly exhibited by concentrated suspensions of fine solid particles (Perry and Green, 1999). The finite stress required before continuous deformation was 7.2 Pa, and the infinite shear viscosity was 0.023 Pa·s.

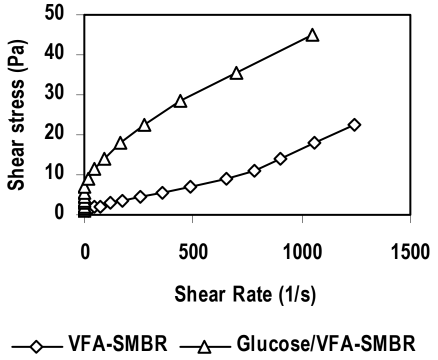

Figure 5.11: Rheological behaviour of the sludge from both AnSMBR, measured at 55 °C and 40 gTSS/L. Analysis were performed at days 142 and 118 of operation of the VFA-SMBR and glucose-VFA-SMBR, respectively.

Temperature affects rheology by affecting the relation between shear stress and shear rate, for both sludge and permeate. Then, it is reasonable to expect higher critical fluxes at higher temperatures. Indeed, results presented in Chapter 2 shows the potential benefits of a thermophilic operation over the critical flux value, in comparison with mesophilic conditions. Latter results were obtained, however, based on short term experiments. On days 149 and 150 of the operation of the VFA-SMBR, two series of critical flux measurements were conducted, at 30 and 55 °C, by adjusting the reactor temperature. Results are presented in Figure 5.12. Critical flux values for both temperatures are coincident. Cake formation when operating the VFA-SMBR over the critical flux, expressed as resistance increase rate, is also the same (Figure 5.12B). This means that the previously observed benefits of a higher operation temperature are not longer observed in long term continuous operation. Hence, the critical flux is fully determined by the properties of the sludge, particularly the fraction characterized by a small particle size. Indeed, long term fluxes observed in the mesophilic AnSMBR described in Chapter 4 were unexpectedly 2-3 times higher than those attained under thermophilic conditions. Apparently, the physiological effects of temperature on the properties and composition of the sludge are much more important for membrane filtration than the physical effect of temperature on sludge rheology.

The low operational fluxes attained during the operation of the glucose/VFA-SMBR are most likely also related with particle size. However in the case of this reactor the important growth of acidogenic bacteria seemed to be additionally responsible for the poor filtration performance. Light microscopy observations suggested that the acidogenic bacteria grew to a high extent as individual cells, and not in flocs. In order to asses the effect of acidogenic bacteria on the filtration performance of the glucose/VFA-SMBR, at the end of the reactor operation the sludge was separated in 2 fractions by a gentle centrifugation (2500 rpm for 5 minutes). Particle size distribution analysis of both fractions is presented in

Figure 5.13. When this separation was performed, reactor solids concentration was 39 g TSS/L. The fraction with smaller particles (supernatant after centrifugation) represented 46% of the solids of the reactor. Activity determinations performed with the centrifugation supernatant revealed no methanogenic activity and an acidogenic activity close to 7 g-glucose/g VSS·d.

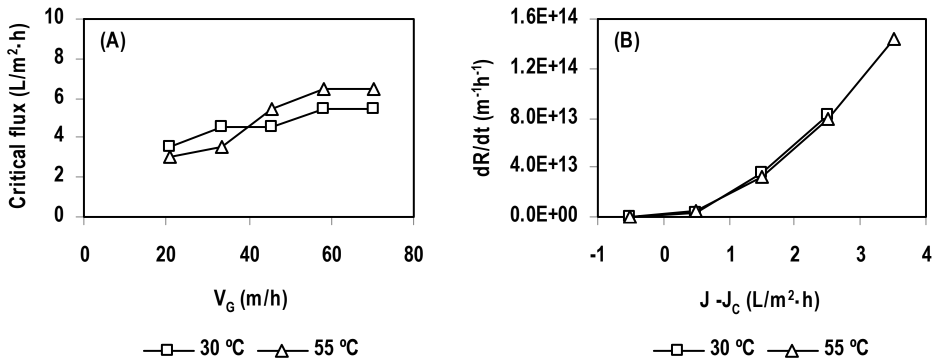

Figure 5.12. Effect of temperature on critical flux and supra-critical cake formation rate on the VFA-SMBR. (A) Critical flux measured at 30 and 55 °C, at different values of V_G. (B) Resistance increase rates (dR/dt) when operating over the critical flux, at V_G 70 m/h.

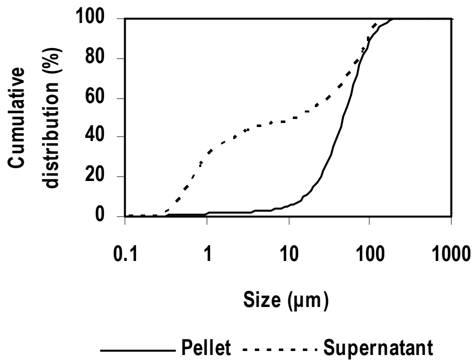

Figure 5.13. Cumulative particle size distribution of the two sludge fractions from the glucose/VFA-MBR, separated by centrifugation.

In order to asses the effect of this fraction of acidogenic bacteria on the filtration flux and resistance, 3 series of critical flux measurements were performed:

- S1: performed with the original sludge from the glucose/VFA-SMBR, at a solids concentration of 39 g TSS/L (before the separation by centrifugation took place).

- S2: performed with the original sludge from the glucose/VFA-SMBR, but at 21 g TSS/L, to match the solids concentration of S3 (before the separation by centrifugation took place).
- S3: performed with the glucose/VFA-SMBR sludge, after removing the supernatant from the centrifugation process. Solids concentration was 21 g TSS/L.

Critical flux measurements were performed at five different values of V_G. Results are presented in Figure 5.14. Cake formation rates at the highest V_G are also presented (Figure 5.14B). The critical flux measurements were performed at different biomass concentrations, and in some cases critical fluxes greatly differ from each other. In order to correctly compare cake formation rates, they have been expressed as the $\alpha \cdot K$ product. Here, α represents the specific cake resistance, and K is a factor that accounts for the cross-flow effect. K equals one under dead end filtration, and zero when no cake formation takes place. A description regarding the evaluation of this parameter can be found in Chapter 2. Removal of the centrifugation supernatant from the reactor resulted in an important increase of the critical flux, and a dramatic decrease in the cake formation rate, showing that the presence of this fraction in the glucose/VFA-SMBR greatly determined the attained flux. Indeed, when this fraction was present, even a decrease by almost 50% in solids concentration produced almost no effect on the critical flux (S1 and S2 in Figure 5.14). This result clearly indicates that the degree of wastewater acidification can strongly determine the physical properties of the sludge developed in an AnSMBR, consequently determining the applicable flux.

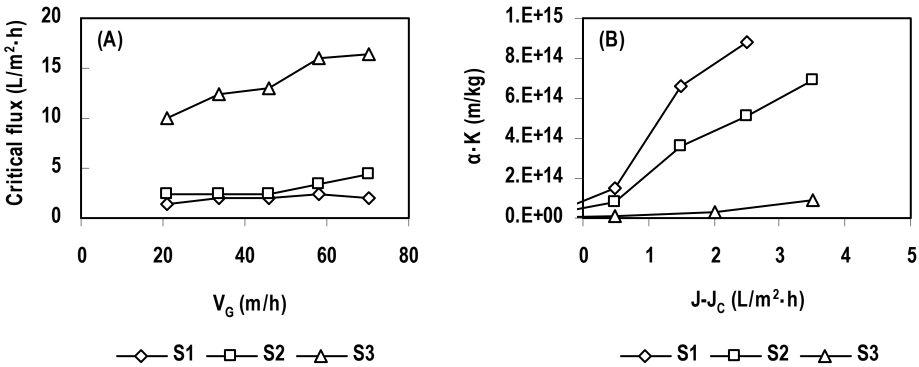

Figure 5.14. Critical flux measurement of different sludge fractions separated by centrifugation. (A) critical flux values, (B) cake formation rates over the critical flux at a V_G of 70 m/h.

Specific cake resistance was measured using the sludge from the glucose/VFA-SMBR, and the centrifugation supernatant, containing a high concentration of acidogenic bacteria. Results were $4.4 \cdot 10^{14}$ and $6.2 \cdot 10^{14}$ m/kg, respectively. Figure 5.14B presents values of the $\alpha \cdot K$ product, which are higher than the respective values of α. It should be noted that $0<K<1$. This means that the properties of the cake formed during the reactor operation are different than those of the cake formed under dead-end filtration. This phenomenon has also been recently reported for aerobic submerged MBRs (Wang et al., 2007). The higher resistance of the cake layer formed during AnSMBR operation can be explained by the segregation of smaller particles induced by their lower back-transport. As already discussed, if surface shear is applied over the membrane, smaller particles will undergo lower back-transport, resulting in a preferential deposition, generating a cake with higher specific resistance. This explains why the properties of a fraction of the reactor solids can indeed determine the overall performance of the entire reactor.

5.3.2. Economic feasibility of AnSMBR

The application of membrane separation processes to anaerobic digestion for wastewater treatment involves additional costs. The most important ones are those related with the membranes themselves and the cost of the energy required for gas sparging. The costs of membrane acquisition and replacement, in € per unit of permeate, depends on the membrane price (in €/m^2), the applied flux and the membrane lifetime, and can be evaluated as follows:

$$\text{Membrane costs} = \frac{\text{Membrane price}}{\text{Flux} \cdot \text{Membrane lifetime}} \qquad (4)$$

Energy requirements for gas sparging depends on the applied V_G, membrane packing, and hydrostatic head. Figure 5.15 shows the membrane costs and energy costs for gas sparging, expressed per m^3 of permeate. The following assumptions have been made: membrane lifetime: 5 years, hydrostatic head: 4 m, compressor efficiency: 60%, electricity price 0.06 €/kW·h. Power requirement for gas pumping was evaluated assuming biogas adiabatic compression (Judd, 2006). Membrane packing was evaluated considering 2 m long vertical tubular membranes, 0.9 cm diameter, with 50% of free transversal area. Three membrane prices have been considered: 150, 100 and 50 €/m^2. Energy requirement for gas sparging was evaluated considering a V_G of 100 m/h, which corresponds to the maximum value tested in this research. Theoretical energy requirement value was increased in 50% to account for frictional losses.

Figure 5.15 shows that for AnSMBR applications the membrane itself represents a much more important economic factor than energy, even when low membrane prices are considered. Costs are therefore very sensitive to changes in either applicable flux and membrane price. If the flux achieved for the VFA-SMBR is considered (7 L/m^2·h), membrane requirements would involve a cost close to 0.33 € per m^3 of treated wastewater, for a membrane price of 100 €/m^2. Even though membrane price has experienced a dramatic decrease during the last decade (Judd, 2006), it still represents a much more important economic factor than energy. Energy requirements for gas sparging are only 0.05 €/m^3 at a V_G of 100 m/h. Membrane requirement and its high related cost may therefore restrict the potential application of submerged membranes. On the other hand, the low energy requirement of AnSMBR systems would allow for an increase in the gas sparging rate to higher levels, with only a low impact on the overall cost. However, during the present research the increase in gas sparging rate was ineffective in achieving high levels of critical flux.

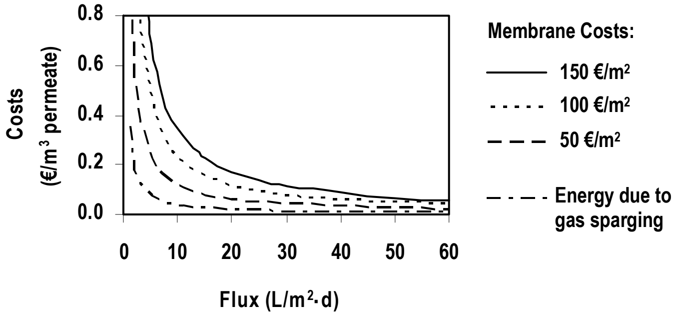

Figure 5.15. Membrane costs and gas sparging costs for submerged membrane bioreactors, considering three different membrane prices. See text for assumptions.

5.3.3. Alternatives to increase surface shear

Previously discussed results clearly show that the application of submerged membranes to thermophilic anaerobic digestion is limited by particle deposition over the membrane surface. Gas sparging under a submerged configuration fails to provide sufficient surface shear to achieve neither moderate nor high levels of flux. Other configurations, that can provide the required level of surface shear to restrict cake formation, need to be evaluated. The use of three phase slug flow in inside-out tubular membranes have been reported to enhance microbial microfiltration processes (Lee et al., 1993; Mercier et al., 1998). It has also been applied to aerobic membrane reactors with positive results (Cui et al., 2003). Secondary flows generated by rising bubbles enhance wall liquid mass transfer coefficients, reducing the chances for particle deposition. Mass transfer is especially high in the film zone, and in the subsequent the bubble wake (Ghosh and Cui, 1999). On the other hand, high liquid cross-flow velocity is a common way to provide high levels of surface shear.

Figure 5.16 presents critical flux determinations for the 3 tested configurations: (A) a submerged membrane with gas sparging, (B) a gas slug flow in inside/out tubular membranes, and (C) a side-stream tubular membrane under high liquid cross-flow. All determinations were performed using the sludge from the VFA-SMBR at a solids concentration of 30 g TSS/L. Figure 5.16A shows the gas sparging effect under the submerged configuration. Values are slightly higher than those presented in Figure 5.9, due to the lower biomass concentration.

Figure 5.16B presents the critical flux determinations under the gas slug flow mode, measured with 2 different membranes. Performance for both membranes is almost the same, even though membranes are very different in terms of material and pore size: ceramic microfiltration and polymeric ultrafiltration membranes. Performance of the slug-flow module is lower than the submerged despite the big differences in V_G. In this research, slug formation was not optimised. Controlling the frequency and length of gas slugs may enhance its effect (Li et al., 1997), but it is unlikely that the performance presented in Figure 5.16B could be distinctly improved.

Finally, Figure 5.16C presents critical flux determinations performed under the side-stream cross-flow configuration. Two values of V_L were tested: 1 and 2 m/s, in presence and absence of gas injection. Preliminary experiments showed that little change in critical flux existed when V_G varied between 5 and 30 % of V_L. Experiments presented in Figure 5.16C have been performed with a V_G that is 10% of V_L. The attained fluxes are several times higher than those obtained with solely gas sparging for particle deposition control. Furthermore, the generation of a three phase flow inside the membrane produced an important increase in the critical flux. Sludge viscosity at 55 °C was close to 0.01 Pa·s, which means a Reynolds number of 1250, at a V_L of 2 m/s, indicating a laminar flow regime. Apparently, the inclusion of gas significantly increased the turbulence, which in turn is likely to be the reason for the increase in critical flux. At values of V_L and V_G of 2 and 0.2 m/s, respectively, a critical flux of 68 L/m²·h was measured, a value that is one order of magnitude higher than those observed with only gas sparging.

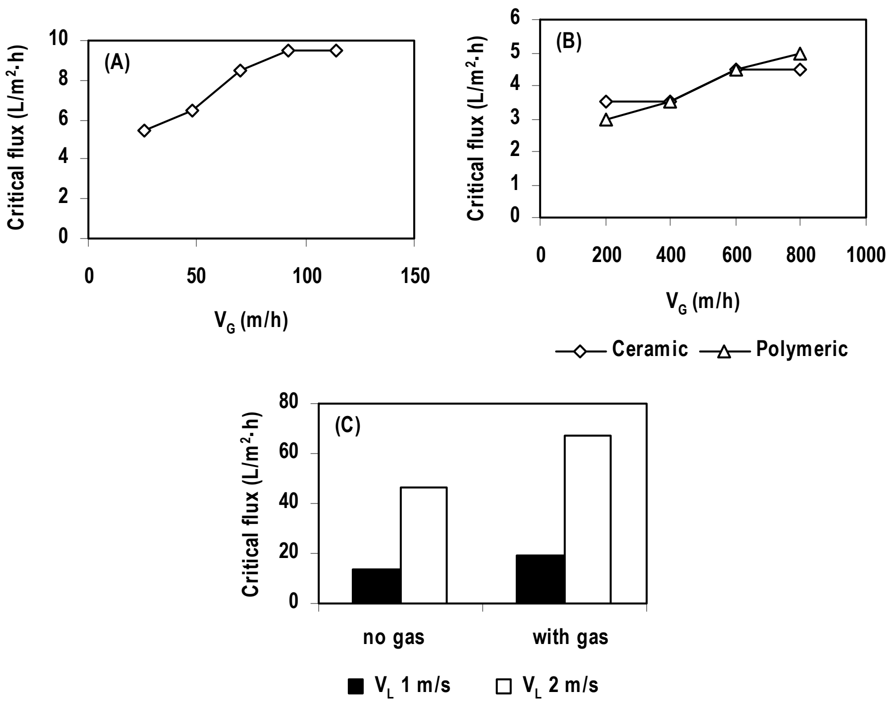

Figure 5.16. Critical flux determination under different membrane configurations of the VFA-SMBR: (A) submerged outside-in membrane. (B) External inside-out membranes under gas slug flow conditions. (C) External cross-flow configuration (V_G was 10% of the V_L). Solids concentration in all tests was 30 g TSS/L.

The critical flux values presented in Figure 5.16C are the result of short term experiments. Cross-flow conditions were applied for only some hours. Under long term operation, a decrease in particle size is likely to occur, which may affect the observed values of critical flux. However, the huge difference between flux values obtained under solely gas sparging conditions, in comparison to cross-flow filtration, suggests that a cross-flow configuration may be more adequate. Experiences with aerobic MBRs indicate that a side-stream configuration could increase energy requirements by more than one order of magnitude (Gander et al., 2000). However, if this option can indeed provide significantly higher fluxes, the reduction in membrane requirements may compensate the increase in energy costs. Long term operation is however required in order to determine the feasibility of the application of cross-flow membrane filtration to thermophilic anaerobic digestion processes.

5.4. CONCLUSIONS

The applicable flux in thermophilic AnSMBR is mainly limited by cake formation over the membrane surface, irrespective of the degree of substrate acidification. Membranes seem to be subjected to low levels of irreversible fouling. Even though cake formation is mainly reversible, high TMP increase rates when the critical flux is exceeded, restricts the operation to a range close to the critical flux. The degree of wastewater acidification significantly affects physical properties of the sludge, greatly affecting the attainable flux.

The properties of the solids forming the cake layer when applying a flux over the critical value can differ from the solids in the bulk of the reactor. This is likely caused by the segregation induced by the different back-transport magnitudes on the particles comprising the sludge. The latter means that the properties of a specific fraction of the sludge can determine the behaviour of the full system.

Since reversible cake formation was identified as the limiting factor for the operational flux, increasing surface shear should result in higher fluxes. Preliminary tests showed that cross-flow operation may be a feasible alternative to reduce particle deposition. This will be the case only if the high shear stress does not negatively affect the physical properties of the sludge, i.e. inducing a decrease in particle size.

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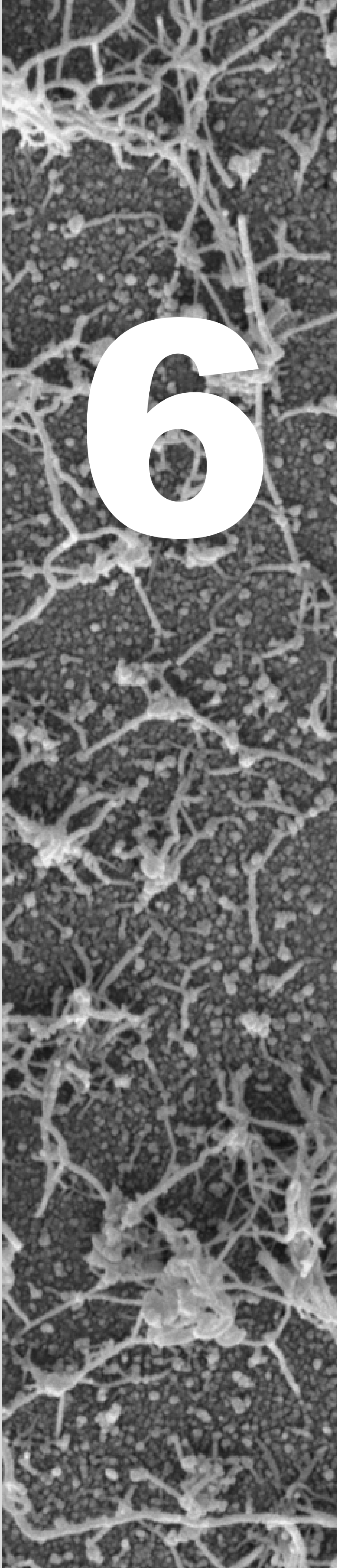
Feasibility of anaerobic membrane bioreactors for the treatment of wastewaters with particulate organic matter



Abstract

The application of anaerobic submerged membrane bioreactors (AnSMBR) was studied for the treatment of high suspended solids content wastewaters. A mesophilic and a thermophilic AnSMBR were operated for 90 days with a synthetic wastewater composed by volatile fatty acids and grinded potato peels as source of suspended solids. Thermophilic AnMBR achieved higher volumetric loading rates than the mesophilic reactor, reaching 14 g COD/L·d, towards the end of the operation, which corresponds to 0.47 g COD/g VSS·d. Mesophilic reactor showed signs of overload, when reaching an volumetric loading rate of 10 g COD/L·d (0.32 g COD/g VSS·d), i.e. accumulation of unconverted solids inside the reactor. Cake formation was identified as the main limiting factor governing the applicable flux. Very low levels of internal pore fouling were observed in both reactors. Very low fluxes were attained, reaching values below 5 L/m^2·h towards the end of the operation. Gas sparging was ineffective in increasing the critical flux values.

6.1. INTRODUCTION

Anaerobic digestion is nowadays an established technology, successfully used to treat a wide range of industrial and domestic wastewaters. Apart from its energy requirements, one of the main advantages of anaerobic digestion, in comparison with aerobic treatment, is the low biomass yield. The later is of particular importance for the treatment of high strength wastes, since it leads to a distinctly lower production of surplus sludge. The most important breakthrough in the development of anaerobic technology for wastewater treatment is the application of bioreactors based on biomass immobilization, normally accomplished by granules formation. This strategy results in high microbial biomass concentrations and therefore high treatment capacities. However, the treatment of wastewaters with a high content of suspended solids in granular sludge bed reactors has limitations (Lettinga and Hulshoff Pol, 1991).

Membrane bioreactors (MBR) have generated an increasing interest during the last decade. MBR systems represent a breakthrough technology for wastewater treatment, however their application have been restricted due to high associated costs. Nevertheless, anaerobic membrane bioreactors (AnMBR) are considered an interesting alternative for those situations where success of traditional granular sludge based technologies cannot be ensured. Moreover, AnMBR technology appears highly suitable for the treatment of wastewaters with high content of organic suspended solids, since particulate organic matter is confined inside the reactor.

The application of AnMBRs for the treatment of wastewaters containing high content of suspended solids have been studied using different substrates, such as slaughterhouse effluent (Fuchs et al., 2003), primary or secondary sludge (Pillay et al., 1994; Ghyoot and Verstraete, 1997), cellulose as synthetic substrate (Harada et al., 1994), manure (Padmasiri et al., 2007), with promising results. However, data is still limited on treatment performance and its relation with wastewater characteristics, so further research is needed.

The present research studies the application of membrane assisted biomass retention to the anaerobic treatment of wastewaters which contains a high proportion of particulate organics. Two anaerobic submerged membrane bioreactors (AnSMBR) were operated, under mesophilic and thermophilic conditions. Their performance is evaluated in terms of their loading potential and membrane filtration performance.

6.2. MATERIALS AND METHODS

6.2.1. Reactors setup

Two identical AnSMBR of 3.8 L of useful volume were used to conduct this study. A detailed description of each reactor setup can be found in Chapter 2. Reactors were operated under thermophilic (55 °C) and mesophilic (30 °C) conditions. Both reactors were fitted with identical tubular polysulphone micro-filtration membranes (Triqua, The Netherlands). The membrane modules were composed of 4 tubes of 36.7 and 0.9 cm of length and diameter, respectively, while total membrane area was 0.042 m^2. Biogas recirculation was applied to provide mixing as well as membrane surface shear. The AnSMBRs were operated as gas-lift reactors, with the membranes placed inside the riser. Gas superficial velocities (V_G) have been evaluated considering the free area of the riser.

6.2.2. Reactors operation

The reactors were fed with a synthetic wastewater composed of a volatile fatty acids (VFA) mixture and grinded potato peels as a source of suspended solids. The acetate:propionate:butyrate ratio of the VFA solution was 1:1:1, expressed as chemical oxygen demand (COD). A concentrated VFA solution of 200 g COD/L was fed continuously to the reactors, which was diluted in-line with tap water. Potato peels were fed manually, on a daily basis. Suspended solids particle size was in the range 0.1 to 3 mm. The feeding of potato peels and VFA was performed so both contributed in the same extent to the applied organic loading rate (OLR). The average inlet COD concentration was 10 g/L. When necessary, an oil based antifoaming (Foamtrol AF4030, BetzDearborn NV) was added in order to control excessive foam formation. The AnSMBRs were operated with cycles consisting of 500 seconds of filtration, followed by 15-30 seconds of back-flush. Back-flush was applied by reversing the flow direction, keeping the flux at the same value than during filtration. As a safety measurement, whenever TMP reached 200 mbar, filtration cycle was interrupted and a back-flush was performed. Reactors were inoculated with mesophilic and thermophilic suspended anaerobic sludge coming from previous MBRs operations (Chapters 4 and 5). Initial volatile suspended solids (VSS) concentrations were 35 and 13 g/L for the mesophilic and thermophilic AnSMBR respectively. Reactors were operated at a V_G in the range 70-75 m/h.

6.2.3. Analyses

Total suspended solids (TSS) and VSS were determined according to Standard Methods (APHA et al., 1998). COD was determined using Lange COD cuvette tests (Hach Lange, Germany). VFA were determined in an Hewlett-Packard gas chromatograph (model 5890 series II) with a flame ionization detector (FID), equipped with a column AT Aquawax-DA (Alltech). Proteins were determined by Lowry method, Onishi & Barr modification (Sigma-Aldrich TP0200 total protein kit). Carbohydrates were analysed using a modified anthrone method (Raunkjaer et al., 1994).

The specific methanogenic activity (SMA) was determined as described in Chapter 4, using a neutralized acetate-propionate-butyrate mixture at a COD ratio of 1:1:1 as substrate. An initial substrate concentration of 1.5 g COD/L was applied.

Sludge stability was determined, in duplicates, by the specific amount of methane produced under unfed conditions over a period of 100 hours. For this purpose, samples of 50 mL of sludge were placed in 250 mL bottles, and the headspace was flushed with a mixture of 80% nitrogen and 20% carbon dioxide, to provide anaerobic conditions. Methane production was followed in time measuring the pressure and composition of the gas in the bottles headspace. The amount of methane, expressed as COD, produced after 100 hours of incubation is reported. This determination represents an indication of the amount of unconverted substrates still remaining in the sludge.

SMA and sludge stability analysis were performed at the same temperature of the corresponding reactors operation: 30 °C for the samples of mesophilic sludge, and 55 °C for the samples of thermophilic sludge.

6.2.4 Apparent membrane resistance and critical flux

Apparent membrane resistance was determined following the procedure already described in Chapter 2. The critical flux was determined applying a flux step method, as also already described in Chapter 2. During critical flux measurements, flux increments of 1 L/m^2·h were applied.

6.3. RESULTS AND DISCUSSION

Figure 6.1 presents the OLR applied to each reactor. Initial volumetric OLRs were different, due to different initial biomass concentrations. However, initial specific OLRs were similar, i.e. about 0.2 g COD/g VSS·d. The OLR of the mesophilic AnSMBR was increased to 10 g COD/L·d on day 26. Sludge wastes were frequently performed between days 15 and 52 to keep TSS concentrations below 40 g/L, as can be seen in Figure 6.2. Effluent COD and reactor soluble COD concentrations remained low up to day 52, when a sharp increase was observed (Figure 6.1). On day 55 permeate COD exceeded 2 g/L, and reactor soluble COD reached 5 g/L. VFA analysis showed that the COD increase was due to accumulation of acetate and propionate acids, in similar proportions. Reactor feeding was stopped on day 55, in order to allow reactor recovery. During mesophilic AnSMBR operation at an OLR of 10 g COD/L·d, 2.3 L of sludge were wasted from the reactor, which equals an overall sludge waste of 77.6 g VSS. If the period of operation at an OLR of 10 g COD/L·d is considered, an apparent yield of 0.080 g VSS/g COD can be evaluated, which is the result of biomass growth and the accumulation of non-degraded substrates. When measuring sludge stability on day 54 a value of 0.30 g COD/g TSS was obtained. Sludge sample for stability measurement was not washed, so the degradation of soluble organic matter present in the sludge also contributed to the value of stability. The high apparent yield and the low sludge stability are indications of reactor overloading; even though permeate COD concentration remained low until day 52. This is due to the fact that the membrane was apparently able to retain the unconverted particulate organics inside the reactor. The high level of sludge wastes performed during the first 55 days of operation most likely resulted in the withdrawal of active methanogenic bacteria. Indeed, SMA decreased from 1.3 to 0.48 g COD/g VSS·d between start-up and day 55.

On day 62 the feeding of the mesophilic AnSMBR was resumed, but with an OLR of 6.3 g COD/L·d, corresponding to 0.32 g COD/g VSS·d. Between days 64 and 77 the observed yield was 0.043 gVSS/g COD, almost 50% lower than the one observed at the OLR of 10 g COD/L·d. During the last 10 days of operation (days 80-90), the reactor was fed solely with VFA, keeping the same OLR (6.3 g COD/L·d). During this period, VSS concentration indeed decreased, most likely due to degradation of the accumulated unconverted particulate substrate. The sludge stability at the end of the operation was 0.12 g COD/g TSS.

The behaviour of the mesophilic AnSMBR shows that even though membrane filtration provides a solid free effluent, the reactor capacity is obviously determined by biomass degradation capability. Reactor overloading will produce accumulation of unconverted particulate organic inside the reactor. Eventually, this will lead to an increase in sludge waste frequency and poor surplus sludge stability.

During the operation of the thermophilic AnSMBR, the OLR was gradually increased up to 14 g COD/L·d, as can be seen in Figure 6.1. COD concentrations remained low during most of the operational period (Figure 6.1). An increase in permeate COD and reactor soluble COD was observed between days 22 and 29, and on day 65. This was caused by an accidental increase in the feeding of VFA, due to a setup malfunction. In both cases, the reactor COD dropped to the level prior to malfunction, after few days.

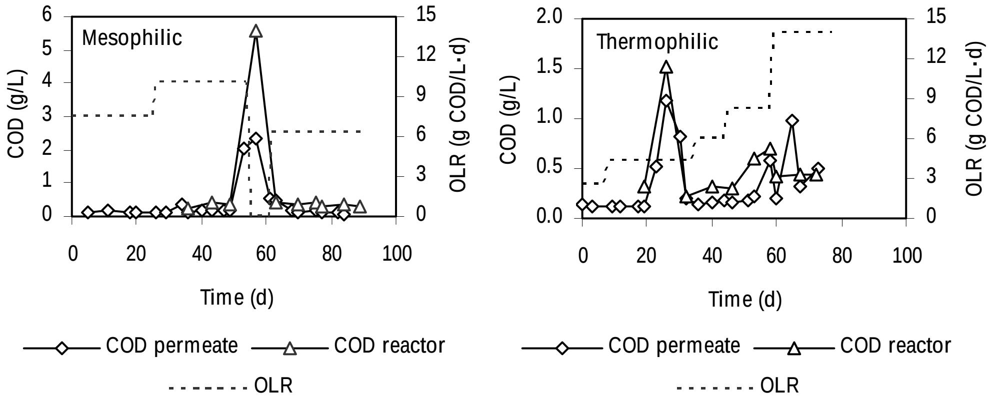


Figure 6.1. Applied OLR, permeate COD and soluble reactor COD during the operation of the mesophilic and the thermophilic AnSMBRs.

The VSS concentration of the thermophilic AnSMBR showed a steady increase from 13 to 30 g VSS/L (Figure 6.2). No sludge waste was performed during the continuous reactor operation. An apparent yield of 0.034 g VSS/g COD is calculated, by using the reactors VSS increase throughout the operation, and the loading rates applied. Sludge stability was measured on days 42 and 75, giving a value of 0.15 g COD/g TSS in both cases. Specific OLR by the end of reactor operation was 0.47 g COD/g VSS·d.

Differences between permeate COD and reactor soluble COD remained in the range of 150-200 mg/L, for both reactors. Accumulation of soluble COD inside AnMBRs bioreactors have been previously reported (Ince et al., 2000). However, no clear tendency was observed during reactors operation regarding the accumulation of soluble COD. During the operation of both AnSMBRs, soluble proteins and carbohydrates in the mixed liquor were generally below 120 and 40 mg/L, respectively.

Figure 6.3 presents the applied flux and filtration resistance during the operation of both reactors. In both cases low fluxes were applied, i.e. in the range of 3 to 6 L/m^2·h. Reactors operation showed to be very unstable, with sudden increases in resistance, as can be seen in Figure 6.3. This was specially the case of the mesophilic AnMBR, forcing to several small adjustments in the applied flux. Very low critical flux values were observed, as can be seen in Figure 6.4. Both reactors experienced a rapid decrease in the critical flux, from 20 to 4 L/m^2·h for the mesophilic AnSMBR, and from 15 to 6 L/m^2·h for the thermophilic AnSMBR.

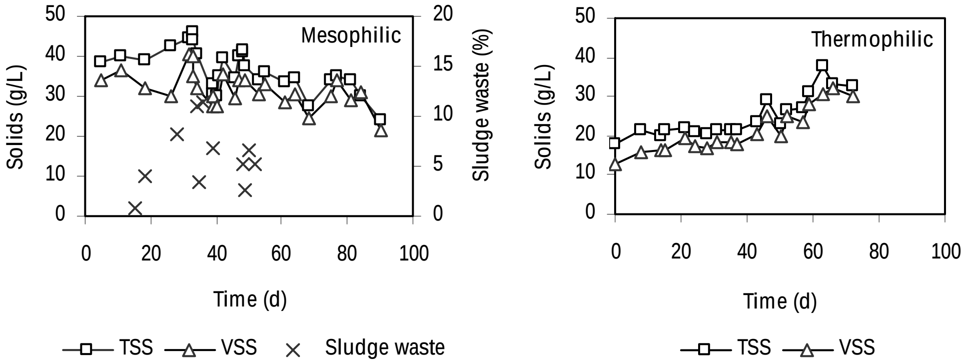


Figure 6.2. TSS and VSS concentrations during the operation of the mesophilic and the thermophilic AnSMBRs. In the case of mesophilic AnSMBR, the volume of wasted sludge is presented as a percentage of the useful volume of the reactor.

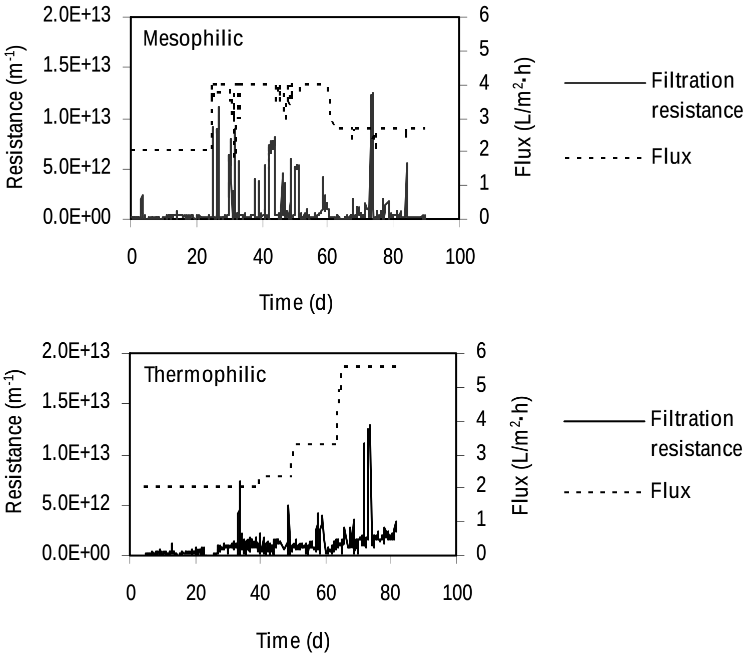


Figure 6.3. Filtration resistance and permeate flux during the operation of the mesophilic and the thermophilic AnSMBRs.

Figure 6.4 also shows that apparent membrane resistance increased during the operation of both reactors. However, it remained below 10^{12} m^{-1}, indicating that a TMP of only 0.022 bar is required as a driving pressure at a flux of 10 L/m^2·h, at 30 °C. At 55 °C, this value is 0.014 bar, due to the lower permeate viscosity. Our results indicate that very low levels of irreversible fouling occurred during the operation of both AnSMBRs. This means that operational fluxes were limited by a reversible process. Cake formation was identified as the limiting factor determining the critical flux. Indeed, resistance increase when critical flux was surpassed showed to be easily reversible by the application of back-flush cycles or permeate collection interruption. This phenomenon was observed during reactor operation and critical flux determination, for both mesophilic and thermophilic AnSMBRs. Our present findings agree with our previous results, presented in Chapters 4 and 5, which showed that during the operation of AnSMBRs with soluble completely acidified wastewaters cake formation is the key factor determining the applicable flux, under both mesophilic and thermophilic conditions.

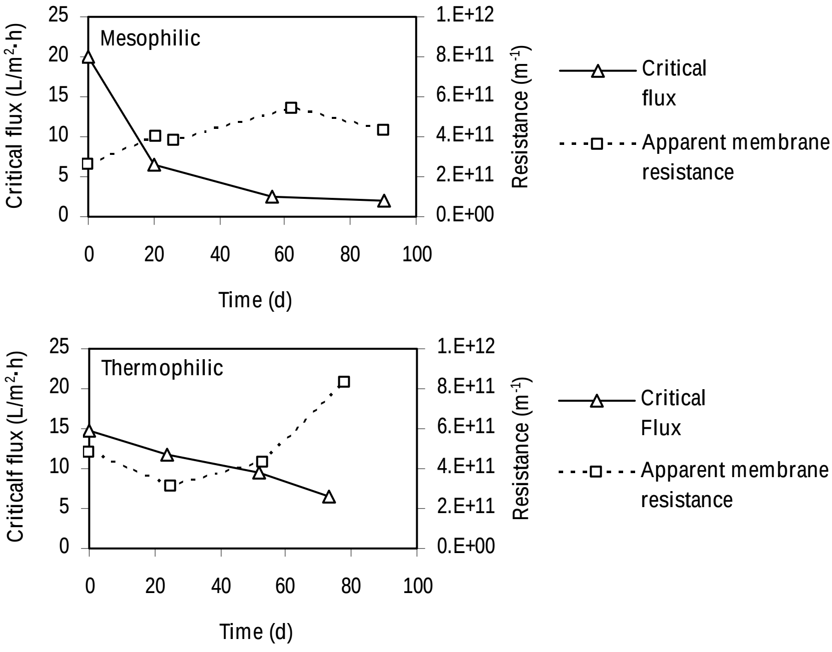


Figure 6.4. Critical flux at a V_G of 70 m/h and apparent membrane resistance, during the operation of the mesophilic and the thermophilic AnSMBRs.

Figure 6.5 presents the effect of V_G on the attainable critical flux, measured several times during the operation of the reactors. The decrease in critical flux in time is evident, as already discussed. At both temperatures, the increase in V_G resulted ineffective in achieving high critical fluxes. In both AnSMBRs, doubling the applied V_G produced an increase in critical flux of only 1-3 L/m^2·h. Apparently, gas sparging was ineffective in generating the high surface shear necessary to control particle deposition, under the conditions of the reactors operation.

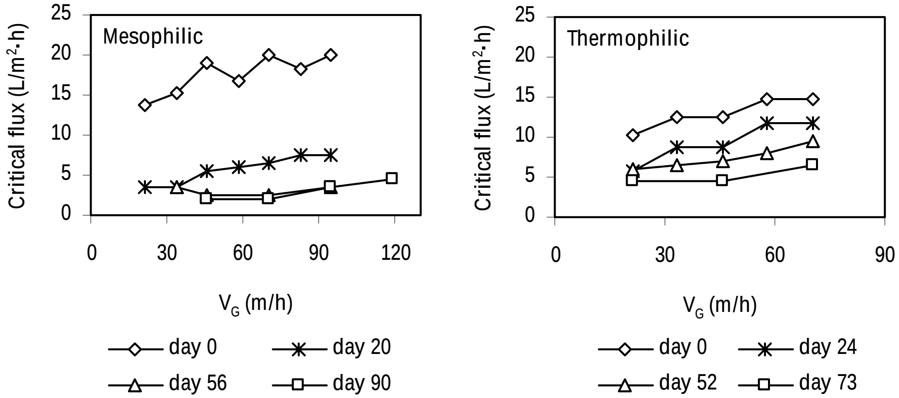


Figure 6.5. Effect of V_G on critical flux, during the operation of the mesophilic and the thermophilic AnSMBRs.

6.4. CONCLUSIONS

Anaerobic MBR technology offers the possibility of total solids retention, enhancing the treatment of particulate organic matter. Furthermore, anaerobic treatment of wastewaters with a high organic fraction of suspended solids can be enhanced applying thermophilic conditions, which provides higher reaction rates and therefore higher organic loading potentials.

Very low levels of irreversible fouling were observed over a 90 days period. Cake formation is the main phenomena limiting the attainable flux. However, gas sparging rate fails to provide enough surface shear to prevent cake formation, when working with tubular membranes in submerged MBRs, at high sludge concentrations.

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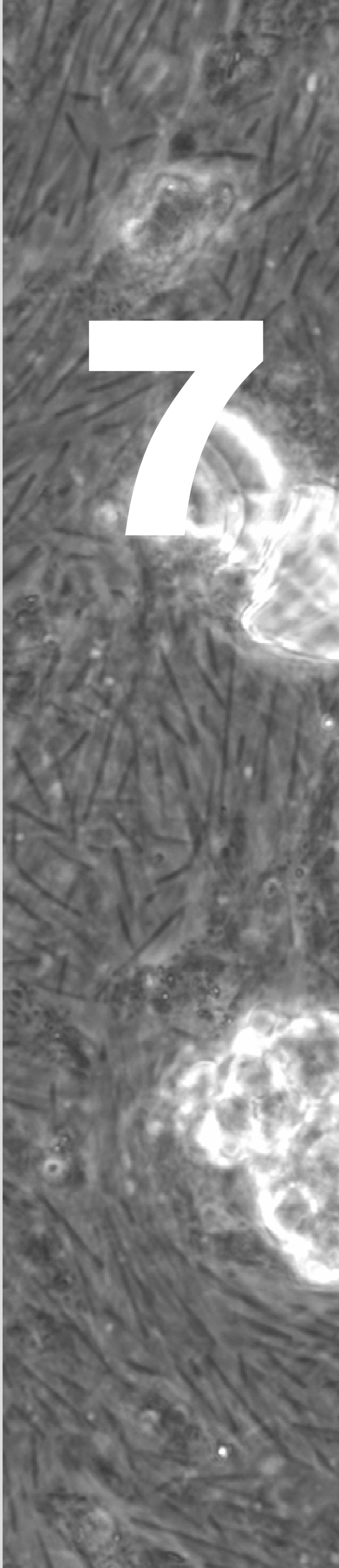

Side-stream thermophilic anaerobic membrane bioreactors: The shear rate dilemma

Abstract

The feasibility of anaerobic side-stream cross-flow membrane bioreactors (CFMBR) was studied under thermophilic conditions, using completely acidified and non acidified substrates. Two CFMBRs were continuously operated at cross-flow velocities up to 1.5 m/s. Cake formation was identified as the key factor limiting the applicable flux, irrespective of the substrate used. Very low levels of irreversible fouling were observed after 200 days of operation. Operational permeate fluxes strongly depended on the level of acidification of the substrates. At similar total solids concentration (28 g/L), the reactor operating with acidified substrates achieved more than twice the flux obtained with the reactor operating with non-acidified substrates. When non-acidified organic matter was used as substrate, the development of acidogenic biomass strongly influenced the physical properties of the sludge, affecting the degree of particle deposition. Under the conditions of this study, no indication was found regarding a possible negative effect of the shear stress generated by the cross-flow liquid velocity on the biological activity via microbial syntrophic conversions. However, exposure of the sludge to a high shear stress affected sludge properties, reducing the attainable flux, most likely due to a reduction of particle size. For comparison, a thermophilic UASB was operated using a VFA mixture as substrate. Results confirmed previous findings showing that biomass retention may limit the performance of granular sludge bed reactors during long term operation.

7.1. INTRODUCTION

Thermophilic anaerobic wastewater treatment offers several potential advantages in comparison with mesophilic processes, such as higher loading potentials, effective removal of pathogenic microorganisms and the elimination of cooling needs when wastewater is already discharged at high temperature (van Lier, 1995; Gerardi, 2003). However, concern exists regarding the efficiency of biomass retention in thermophilic systems (van Lier et al., 1997). Granulation and biofilm formation seems to be more difficult to achieve under thermophilic conditions, in comparison with mesophilic conditions. Moreover, lower net biomass yields are expected under thermophilic conditions, in the range of 50% of those possible under mesophilic temperatures, as the result of higher maintenance requirements and higher decay rates (Zeikus, 1979; Speece, 1996). Membrane filtration represents an alternate way to ensure successful biomass retention under thermophilic conditions. In membrane bioreactors (MBR), biomass is retained independently of its capacity of forming flocs or biofilms, and irrespective of its growth rate or yield.

Considering the position of the membrane with respect to the bioreactor, two main MBR configurations are possible: submerged and side-stream. In the submerged configuration, membranes are submerged in the mixed liquor. In the side-stream configuration, membranes are placed in a circulating loop that connects them with the bioreactor and operated at high cross-flow velocities. In side-stream cross-flow MBRs (CFMBR), higher levels of surface shear are possible, which can be used to reduce the particle deposition over the membrane surface, increasing the applicable fluxes (Beaubien et al., 1996; Elmaleh and Abdelmoumni, 1997; Wisniewski et al., 2000). However, the sludge exposure to high shear conditions may induce a reduction in particle size distribution, increasing the chances of particle deposition (Choo and Lee, 1998). High shear conditions have also been reported as detrimental for anaerobic biomass activity and/or responsible for physical interruption of syntrophic associations, a key factor in the anaerobic degradation of organic matter (Choo and Lee, 1996; Brockmann and Seyfried, 1997; Ghyoot and Verstraete, 1997). However, some authors did not observe apparent problems with metabolic activity when operating anaerobic CFMBRs (Pillay et al., 1994; Fakhru'l-Razi and Noor, 1999; Ince et al., 2001; Fuchs et al., 2003; Padmasiri et al., 2007), most probably as a result of different conditions and setup characteristics.

In principle, operation at high temperatures should be beneficial for membrane filtration due to the effect of temperature on sludge and permeate rheological behaviours. Temperature affects the relation between shear stress and shear rate, which in Newtonian fluids is represented by the viscosity. During the operation of an anaerobic submerged MBR (Chapter 5), attainable fluxes showed to be determined by the development of a fraction of small particles, most likely produced by single cell growth and/or cell decay products. Under these conditions, temperature showed little effect on the attainable fluxes, indicating that the physiological effects of temperature on the properties and composition of the sludge can be much more of importance for membrane filtration than the physical effect of temperature on sludge or permeate rheology. Since permeate flux was mainly limited by reversible cake formation, the surface shear provided by the high cross-flow velocities that characterize CFMBRs should result in an increase in the operational fluxes. This will be the case only if the high shear stress does not negatively affect the physical properties of the sludge, i.e. inducing a decrease in particle size.

An effective way to control trans-membrane pressure (TMP) in anaerobic CFMBRs is through a back-pressure valve located in the circulation line, after the membrane module. However, sludge is exposed to tremendous shear forces when passing this valve. An alternative way of operation is vacuum driven permeate filtration, normally applied in submerged MBRs. However, vacuum driven operation restricts the applicable TMP, since only 1 atm of vacuum is possible. Nevertheless, results from the submerged thermophilic MBR operation (Chapter 5) suggests that if cake formation can be controlled, low values of TMP may be expected. The present research studies the feasibility of vacuum driven anaerobic CFMBRs, in order to reduce the exposure of the sludge to extreme shear forces. Two reactors are operated with completely acidified and non acidified synthetic wastewaters. The operation of a thermophilic upflow anaerobic sludge bed (UASB) reactor fed with acidified synthetic substrate is also presented for comparison purposes.

7.2. MATERIALS AND METHODS

7.2.1. Reactors setup and operation

Three reactors, one UASB and two anaerobic CFMBRs were used to conduct this study. The UASB reactor was 4.5 L of useful volume and was ran prior to the operation of the CFMBRs. The UASB was fed with a partially neutralized volatile fatty acids (VFA) mixture as substrate, with an acetate:propionate:butyrate ratio of 1:1:1, expressed as chemical oxygen demand (COD). The inlet COD concentration was 10 g/L. The UASB reactor was operated applying liquid recirculation in order to provide an upflow liquid superficial velocity in the range of 0.5-0.7 m/h. The reactor was inoculated with mesophilic granular sludge, previously acclimated to thermophilic conditions for two months. Initial volatile suspended solids (VSS) concentration was 17 g/L. Inoculum thermophilic (55 °C) methanogenic activity, determined with a mixture of VFA as substrate, was 0.40 g COD/g VSS·d. The UASB reactor was operated at a temperature of 55 °C.

Two identical anaerobic CFMBRs of 2 L of useful volume were operated, both connected to external membrane modules containing a single tubular membrane. Reactors and membrane modules were equipped with water jackets which were used to keep an operational temperature of 55 °C. Tubular ceramic Al_2O_3 membranes were used (Atech Innovations, Germany), with a pore size of 0.2 μm. Internal and external diameter of the tubular membrane were 6 and 10 mm, respectively. The membrane length was 0.7 m, while the effective membrane filtration area per reactor was 0.013 m^2. Reactors mixed liquor was circulated through the membrane module by means of a peristaltic pump (Masterflex I/P, USA). In order to increase the membrane surface shear, biogas was recirculated and injected inside the membrane tube. No back-pressure valve was placed after the membrane module to control the TMP. Instead, the permeate collection was vacuum driven, by means of a peristaltic pump (Watson Marlow 323U, UK). The system was operated in such a way that the flow of permeate was higher than the reactor influent. Excess permeate was returned to the reactor through an overflowing vessel. TMP was determined measuring the pressure in the membrane module, by a pressure sensor (AE Sensors ATM, The Netherlands). Figure 7.1 presents a schematic representation of the CFMBRs setup. CFMBRs were operated with cycles consisting of 5 minutes of filtration, followed by 20 seconds of back-flush. Back-flush was applied by reversing the flow direction, keeping the flux at the same value than during filtration. During the first days of the CFMBRs operation, permeate flux was fixed at 20 L/m^2·h. Operation then proceeded by controlling the flux in order to keep it in the range of the critical flux according with its weak definition (Wu et al., 1999; Bacchin et al., 2006), using the online tool presented in Chapter 3.

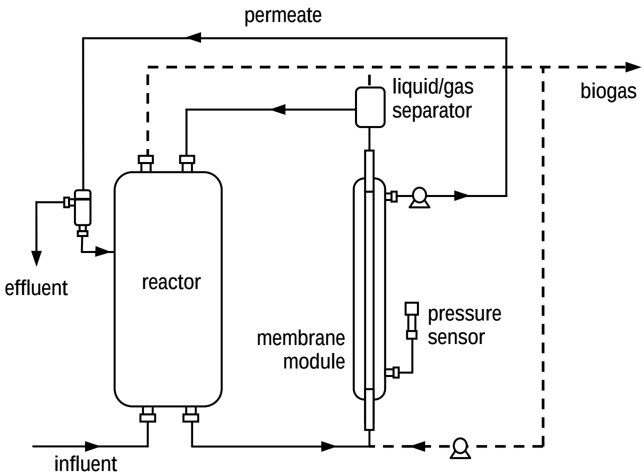

Figure 7.1. Schematic representation of the CFMBR setup. Doted lines indicate gas flows.

Completely acidified and non-acidified synthetic substrates were used to feed the CFMBRs. One of the CFMBRs was operated with the same VFA mixture as the UASB reactor. This reactor will be referred to as VFA-CFMBR. Inlet concentration was 10 g COD/L, which was increased to 20 g COD/L on day 170. The second CFMBR was fed with a non-acidified substrate composed by 40% gelatine, 40% starch and 20% ethanol, percentages evaluated on a COD basis. This reactor will be referred to as NA-CFMBR. The initial inlet concentration was also 10 g COD/L, which was increased to 17 g COD/L on day 155. In both cases, increases in inlet COD concentration were performed in order to allow increments in organic loading rate (OLR), when increases in the inlet flows were not possible for being too close to the actual applied permeate fluxes. CFMBRs were inoculated with a mixed sludge coming from the previously ran thermophilic UASB reactor, and from a thermophilic submerged MBR from a previous study (VFA-MBR described in Chapter 5). Initial biomass concentrations were 6 and 10 g VSS/L for the VFA-CFMBR and the NA-CFMBR, respectively.

7.2.2. Analyses

Total suspended solids (TSS) and VSS were determined according to Standard Methods (APHA et al., 1998). COD was determined using Lange COD cuvette tests (Hach Lange, Germany). Soluble COD was measured after sample filtration through a membrane filter of 0.45 μm pore size (Aqua 30/0.45CA, Whatman, Germany). VFA concentration was determined in a Hewlett-Packard gas chromatograph (model 5890 series II) with a flame ionization detector (FID), equipped with an AT Aquawax-DA column (Alltech). Soluble microbial products (SMP) concentrations were calculated for a given sample as the difference between soluble COD and total VFA concentration, expressed as COD. Permeate viscosities were determined using a capillary U-tube viscometer (Tamson instruments, The Netherlands). Sludge rheology was measured using a rheometer (CVO, Bohlin instruments, UK). CFMBR sludge particle size distribution was measured by laser diffraction analysis (Coulter LS230, Beckman Coulter, USA). The latter particle size data are presented based on volume distributions. Granule size distribution of sludge from the UASB reactor was measured by image analysis according to Jeison and Chamy (1998), based on the individual observation of at least 1500 granules. Granules sizes are presented based on a number distribution. For granular sludge size distribution only particles over 0.15 mm were considered.

The specific methanogenic activity (SMA) was determined as described in Chapter 4, at a temperature of 55 °C. Acetate, propionate, butyrate and hydrogen gas were used as substrates. An initial substrate concentration of 1.5 g COD/L was applied when using VFA as substrate. For SMA determinations using hydrogen gas as substrate, the serum bottles headspace was filled with a mixture of 80% hydrogen and 20% carbon dioxide, at an initial pressure of 1.6 bar. In the latter case, activity was determined following the decrease in pressure, due to hydrogen consumption.

Specific acidogenic activity (SAA) was determined in duplicates in experiments performed in 250 mL serum bottles with 150 mL of media. The same basal medium was used as for SMA determination (Chapter 4). Biomass concentration was 1 g VSS/L. Starch and gelatine were used as sole substrate, at an initial concentration of 1.5 g COD/L. Acidogenic activity was determined as the rate of VFA production in time. Since methane production was detected during the SAA determinations, measured SAA values were corrected by accounting methanogenesis of the acidogenesis products.

7.2.3. Apparent membrane resistance and critical flux determinations

Apparent membrane resistance was determined following the procedure already described in Chapter 2. For this purpose, the membrane module was disconnected from the reactor, rinsed and filled with demineralised water. The critical flux was determined applying a flux step method, as also already described in Chapter 2. During critical flux measurements, flux increments of 2 and 1 $L/m^2 \cdot h$ were applied for the VFA-CFMBR and the NA-CFMBR respectively.

7.2.4. Light microscopy observations

Sludge samples were observed under a Leica DMR light microscope, equipped with a fluorescence unit. The presence of methanogens was detected based on their natural fluorescence.

7.2.5. MBRs filtration performance

In order to comparatively evaluate the filtration performances of both CFMBRs, several critical flux determinations were performed at the end of the reactors operation. Measurements were performed providing the same TSS concentration in each reactor. This required the dilution of the NA-CFMBR sludge and the concentration of the VFA-CFMBR sludge, which were achieved by changing the reactors useful volumes. The applied suspended solids concentration was 28 g TSS/L. The critical flux was determined at liquid cross-flow velocities of 1 and 2 m/s. Determinations were done with and without gas sparging inside the membrane tube. When applied, gas superficial velocity (V_G) was 10% of the applied liquid cross-flow velocity (V_L).

7.3. RESULTS AND DISCUSSION

7.3.1. Biomass retention in the thermophilic UASB reactor

Figure 7.2 presents the applied loading rate and effluent VFA concentration during the operation of the thermophilic UASB reactor, fed with VFA as substrate. During the first days of operation, a high VFA concentration was preset in the effluent, however, it dropped to a lower level as the operation proceeded. OLR was increased during the first 100 days by reducing the hydraulic retention time. From day 100 onwards, OLR was fixed at 25 g COD/L·d. Total VFA concentration remained low after day 100, most of the time below 300 mg COD/L. On day 168 a water-bath failure caused a decrease in the reactor temperature to 30 °C for a period of 24 h, which caused a temporary VFA increase in the reactor effluent.

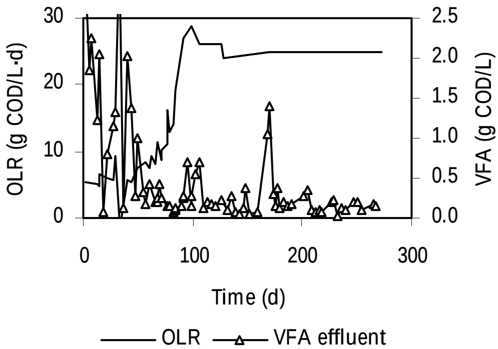

Figure 7.2. Applied OLR and effluent VFA concentration during the operation of the thermophilic UASB.

Sludge SMA increased during the first part of the UASB reactor operation, and then remained approximately constant, as can be seen in Figure 7.3. By the end of the operational period, acetotrophic SMA reached 2.2 g COD/g VSS·d. However, observed hydrogenotrophic SMA remained surprisingly low, suggesting that acetoclastic methanogenesis was the main route for acetate conversion. However, it must be considered that hydrogenotrophic methanogenic activity may be underestimated due to mass transfer restrictions, since during SMA determination hydrogen must be transferred from the gas to the liquid phase, and then diffuse inside the microbial flocs. Effluent VSS concentration were in the range of 100 to 250 mg/L most of the operational period. Washed-out solids showed extremely high SMA values, as can be seen in Figure 7.3. The UASB reactor was started up with an initial biomass concentration of 17 g VSS/L. By the end of the operation, the biomass concentration was 15.3 g VSS/L, which represents a decrease of 10% with respect to the initial value. The decrease in retained biomass is most likely related with the low apparent yield of thermophilic anaerobic sludge and the wash-out of active thermophilic microorganisms. Granule size distribution showed a decrease during the reactor operation as can be seen in Figure 7.4. Average particle size decreased from 1.2 to 0.86 mm. Smaller granule sizes usually involve lower settling velocities and therefore higher chances of wash-out. Considering the fact that mixing conditions in full-scale reactors are much more severe than those present in lab-scale reactors, one could speculate that more intense biomass wash-out occurs in upscale thermophilic systems.

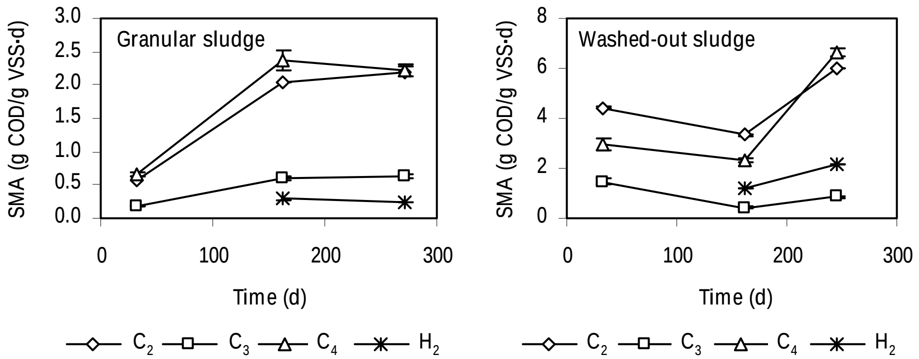

Figure 7.3. SMA measured with acetate (C_2), propionate (C_3), butyrate (C_4) and hydrogen (H_2) as substrates of the granular sludge and washed-out sludge, during the operation of the thermophilic UASB reactor. Error bars represent the standard deviation between duplicates.

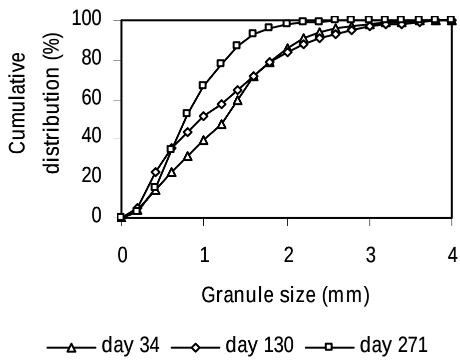

Figure 7.4. Cumulative particle size distribution of the granules from the UASB reactor.

Our results indicate that inefficient sludge retention may limit the long term operation of high rate thermophilic anaerobic granular reactors, treating acidified wastewaters. In such case, enhanced biomass retention by membrane filtration may then represent a positive feature for the feasibility of anaerobic thermophilic treatment.

7.3.2. CFMBRs operation

The solids concentration increased in both reactors throughout the operation. From day 140, periodic sludge wastes were applied to the NA-CFMBR, in order to keep a sludge age of around 120 days. The same was done in the VFA-CFMBR starting on day 160. By the end of the operation, solids concentrations were 41 g TSS/L (38 g VSS/L) for the NA-CFMBR, and 24 g TSS/L (21 g VSS/L) for the VFA-CFMBR.

Figure 7.5(A) presents the applied OLR and permeate VFA concentration during the operation of the VFA-CFMBR. Applied OLR was increased during the first 50 days reaching 30 g COD/L·d. On day 53 a failure in the permeate pump produced the accidental wash-out of part of the reactor biomass. OLR was reduced to 10 g COD/L, and then continuously increased up to 45 g COD/L during the following days. On day 100, a pH drop to 5.5 was observed in the VFA-CFMBR, due to reactor overloading. As a curative measure, the OLR was reduced to allow recovery. Between days 100 and 140, propionate concentrations were in the range 250-600 mg/L, being the main compound contributing to the total VFA concentration. In order to allow a further increase in OLR, keeping permeate VFA concentration to the minimum, propionate contribution to influent COD was decreased from 33% to 20% (on COD basis) on day 140. The latter enabled the increase in OLR up to 55 g COD/L·d, towards the end of the operation. Figure 7.5(B) presents the applied and removed propionate loading rates during the operation of the VFA-CFMBR. Propionate loading rate was around 10 g COD/L·d by the end of the operation, most of which was successfully converted. This conversion capacity agrees with the observed SMA measured with propionate as substrate, presented in Figure 7.6. SMA with propionate as substrate was 0.7 g COD/g VSS·d, which multiplied by the biomass concentration (21 g VSS/L) represents 14.7 g COD/L·d for the entire reactor system.

SMA for the four tested substrates increased during the operation, with the exception of propionate which remained constant (Figure 7.6). The latter may have been the result of the reactor acidification occurred on day 100, which particularly affected propionate oxidation. SMAs measured at the end of the VFA-CFMBR operation were higher than those measured at the end of the UASB operation (Figure 7.3), for all substrates. This, most likely, was the result of the combination of different factors: enhanced biomass retention, the reduction of the mass transfer limitations due to the absence of granules and the higher applied loading rates resulting in a higher biomass growth. Reactor performance and sludge SMAs clearly show that propionate oxidation is the limiting factor for the treatment of acidified wastewaters. Propionate oxidation has been recognised as a limiting factor in thermophilic degradation of organic matter (van Lier, 1995; Speece *et al.*, 2006), so this behaviour does not represent a particular result of the cross-flow operation of the VFA-CFMBR. Therefore, it is not evident that this limitation is the result of a negative effect of the shear stress on the biological activity of the sludge.

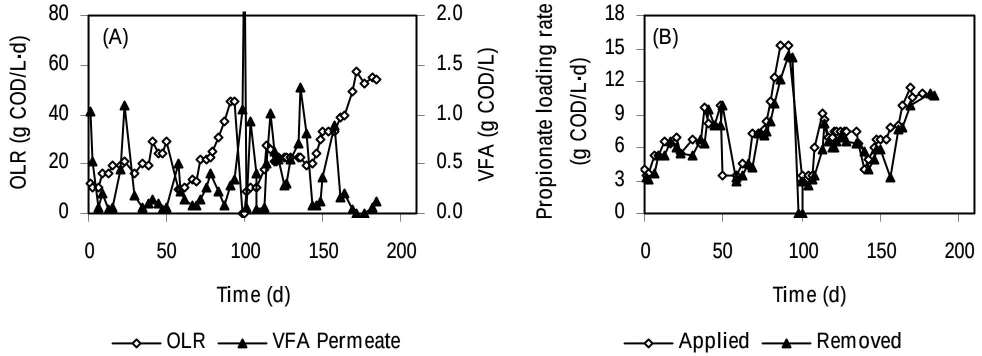

Figure 7.5. (A) Applied organic loading rate and permeate VFA concentration during the operation of the VFA-CFMBR. (B) Applied and removed propionate loading rates during the operation of the VFA-CFMBR.

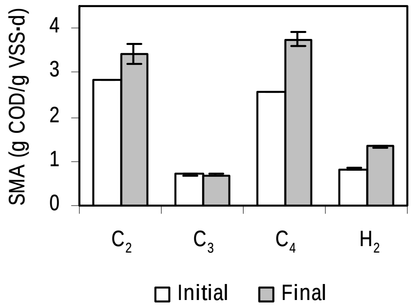

Figure 7.6: SMA measured with acetate (C_2), propionate (C_3), butyrate (C_4) and hydrogen (H_2) as substrates for the VFA-CFMBR sludge at the beginning and the end of the reactor operation. Error bars indicate the standard deviation between duplicates.

The applied OLR on the NA-CFMBR is presented in Figure 7.7(A), together with the effluent VFA and COD concentrations. The OLR varied between 10 and 15 g COD/L·d, during most of the operational period. When increasing the OLR to 15 g COD/L·d on day 154, a growing accumulation of VFA was observed, which demanded an OLR reduction to 10 g COD/L·d on day 187, in order to achieve system recovery. Propionate accumulation was responsible for the majority of the observed VFA increase between days 160 and 195, as can be seen in Figure 7.7(B), which shows the effluent propionate contribution to total the VFA concentration. Figure 7.7(A) also shows the presence of non-VFA COD in the reactor effluent, probably soluble microbial products (SMP) or non-converted substrates.

Figure 7.8 shows a decrease in SMA during NA-CFMBR operation, for all the tested substrates, with the exception of that measured using hydrogen as substrate. This decrease can be explained by the growth of acidogenic bacteria that “dilutes” methanogenic and acetogenic microorganisms, and by the overall adaptation to the substrates and loading conditions. The latter most likely explains the big decrease in the SMA based on butyrate, as the inoculum sludge was fed with a relatively high butyrate load, a compound that was not directly fed during the operation of the NA-CFMBR. The SMA on propionate was 0.31 g COD/g VSS·d. The latter value is in the same range of other values reported in literature, when applying thermophilic anaerobic treatment to non-acidified or partially acidified wastewaters (Syutsubo et al., 1997; Syutsubo et al., 1998; Fang and Chung, 1999; Yamada et al., 2006). Our results show no clear indication that cross-flow conditions were especially harmful for propionate oxidation during the operation of the NA-CFMBR, even though the propionate accumulation was the main factor restricting the applicable loading rate.

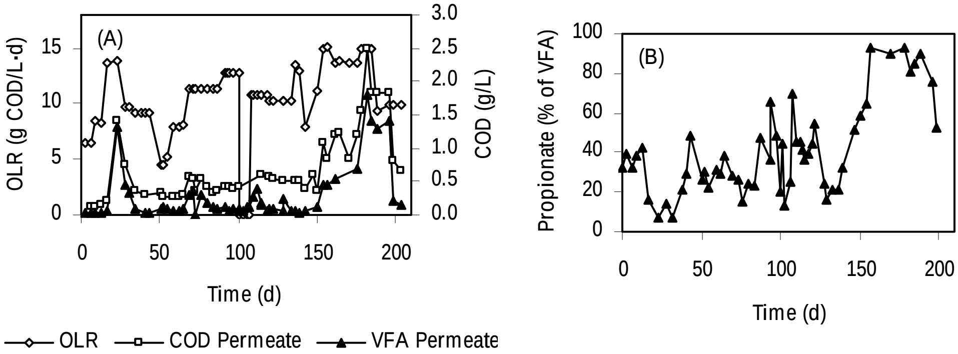

Figure 7.7. (A) Applied organic loading rate and effluent COD and VFA concentrations during the NA-CFMBR operation. (B) Effluent propionate contribution to total VFA concentration, expressed as percentage (COD basis).

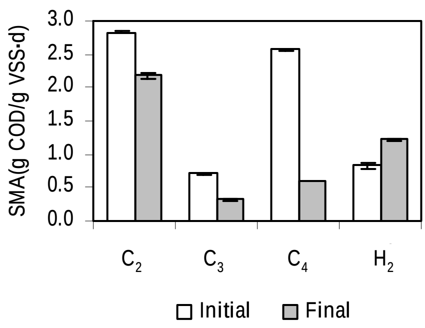

Figure 7.8: SMA measured with acetate (C_2), propionate (C_3), butyrate (C_4) and hydrogen (H_2) as substrates for the NA-CFMBR sludge at the beginning and the end of the reactor operation. Error bars indicate the standard deviation between duplicates.

Several authors have identified strong mixing conditions as a detrimental factor for propionate degradation, since it supposedly affects microbial proximity and therefore syntrophic hydrogen transfer (McMahon et al., 2001; Kim et al., 2002a; Speece et al., 2006). However, syntrophic relations are obviously established at a microscopic rather than at a macroscopic scale. Therefore bulk conditions and/or concentrations may not correctly represent the actual conditions to which microorganisms are actually exposed to.

Both MBRs showed an accumulation of SMP inside the reactors, but at very different levels, as can be seen in Figure 7.9. In the case of the VFA-CFMBR, this accumulation was related with the applied OLR, a phenomenon that was also observed by Ince et al. (2000), when operating an anaerobic CFMBR with brewery wastewater. The NA-CFMBR presented very high concentrations of SMP in the reactor, reaching almost 14 g COD/L around day 140. When sludge waste started on the latter day, the SMP concentration decreased and stabilized around 6-7 g/L. From day 101 till 107, the substrate feeding to the NA-CFMBR was stopped. During the latter period, the reactor soluble COD practically did not vary, indicating that the observed accumulated COD was not unconverted substrate, but recalcitrant SMP produced within the reactor. SMP accumulation in mesophilic anaerobic MBRs has been previously observed (Ince et al., 2000; Aquino et al., 2006). The higher level of SMP in the NA-CFMBR in comparison with the VFA-CFMBR is most likely related with its complex substrate, which involves a higher microbial variety and diverse degradation intermediates.

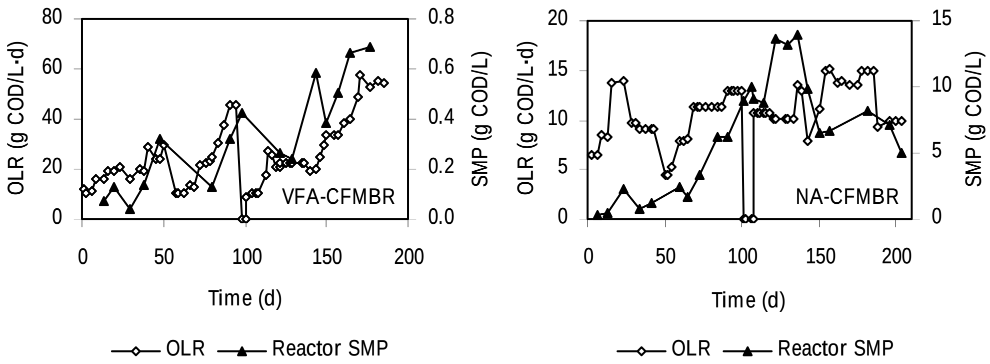

Figure 7.9. Applied organic loading rate and reactor SMP during the operation of the CFMBRs.

7.3.3. Filtration performance of side-stream MBRs

Figure 7.10 presents the cross-flow velocities and permeate flux applied during the continuous operation of the VFA-CFMBR, along with the observed filtration resistance. Figure 7.11 shows the same data, for the NA-CFMBR. Applied V_L varied between 1 and 1.5 m/s for both CFMBRs. When applied, gas injection in the membrane tube was applied at a V_G of 0.1 m/s.

Permeate fluxes in the VFA-CFMBR varied between 20 and 40 L/m^2·h, depending on the imposed operational conditions. On day 165, a failure in the PC responsible for the reactors control produced an accidental operation of the VFA-CFMBR at a flux of 50 L/m^2·h, a value much higher than the critical flux, during two days. After the latter incident, the membrane was physically cleaned on day 167, and the operation was restarted. Physical cleaning consisted of the physical removal of the cake layer from the membrane surface, using a soft wool brush to gently scour the inner surface of the membrane tube. Cake formation was identified as the main factor limiting the flux of the VFA-CFMBR, since fast increases in TMP where observed when surpassing the critical flux, and permeability was easily recovered by the application of a short back-flush cycle (20 seconds). Indeed, only low levels of irreversible fouling were observed during the operation of the VFA-CFMBR, as evidenced by the low values of the apparent membrane resistance (Figure 7.12). The apparent membrane resistance showed a clear increase after the already mentioned accidental operation at a flux of 50 $L/m^2{\cdot}h$. However, the physical cleaning operation performed on day 167 resulted in an almost complete recovery of the membrane permeability. Since physical cleaning is a superficial treatment, it removes material deposited over the membrane surface. Its high efficiency clearly indicates that cake consolidation, and not irreversible fouling, was the phenomenon responsible for the high apparent membrane resistance measured on day 167. The applied flux showed a moderate reduction during the operation of the VFA-CFMBR (Figure 7.10). A flux of around 35 $L/m^2{\cdot}h$ was applied during the first month of operation at a V_L of 1 m/h. The latter value was reduced to below 30 $L/m^2{\cdot}h$, at a V_L of 1.5 m/h, with gas injection. This stabilization at a lower level is most likely the result of the increase in solids concentration and the change in sludge properties due to sludge exposure to shear forces.

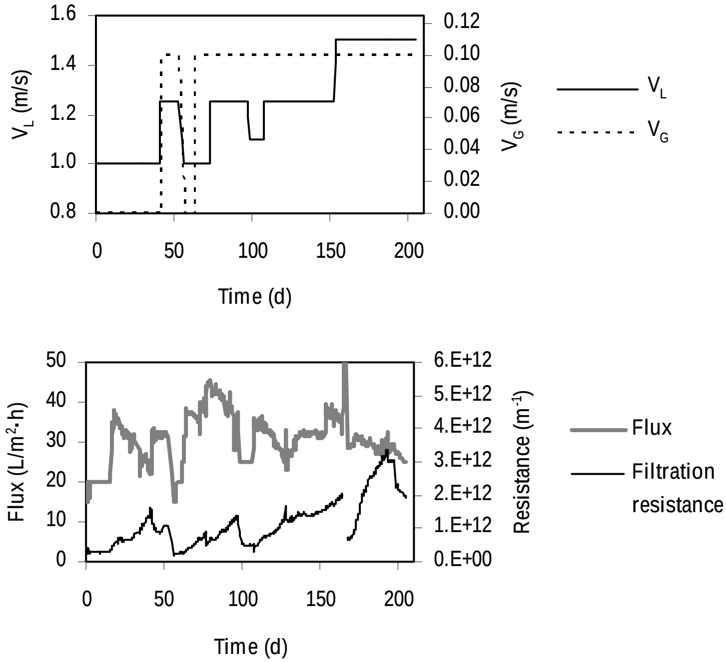

Figure 7.10. Applied V_L, V_G, flux and measured filtration resistance during the operation of the VFA-CFMBR.

During the operation of the NA-CFMBR, the applied flux showed a fast decrease during the first 50 days of operation, as can be seen in Figure 7.11. On day 170 the permeate flux was fixed to a constant value of 6.5 $L/m^2 \cdot h$, a value slightly over the critical flux, which produced an increase in filtration resistance during the last 30 days of operation. Significant changes in sludge physical properties were observed during the first 60 days of operation, which coincides with the period of flux decrease. Sludge apparent viscosity increased, and the development of an important fraction of acidogenic bacteria was detected. This behaviour was also observed during the operation of the thermophilic submerged MBR operated with a partially acidified synthetic wastewater (glucose/VFA-SMBR), described in Chapter 5. During the operation of the latter reactor, the development of acidogenic bacteria was recognized as an important factor determining the applicable fluxes. Reversible cake layer formation was identified as the limiting factor for the applied flux during the operation of the NA-CFMBR. Even though apparent membrane resistance showed a slow increase during reactor operation, it remained below $6 \cdot 10^{11}$ m^{-1}, indicating low levels of irreversible internal pore fouling (Figure 7.12).

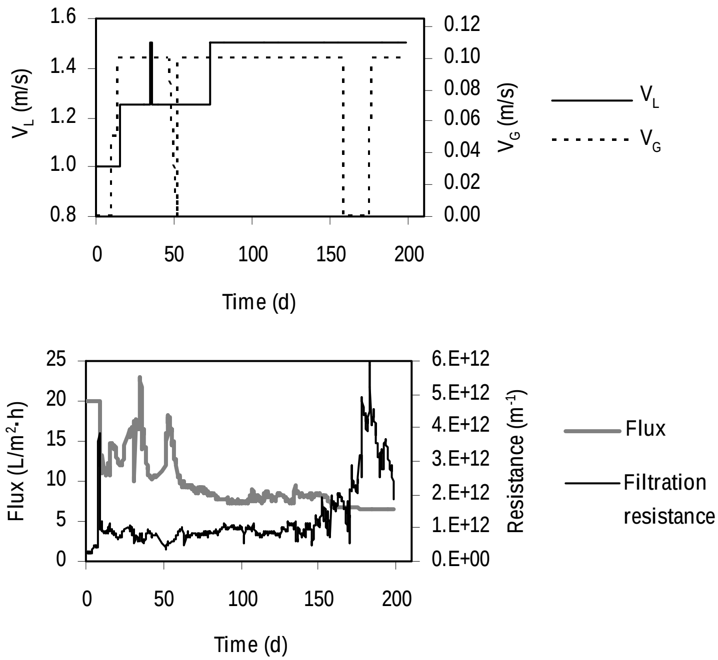

Figure 7.11. Applied V_L, V_G, flux and measured filtration resistance during the operation of the NA-CFMBR.

Figure 7.13(A) presents the results of the critical flux measurements performed at the end of the VFA-CFMBR operation. At a V_L of 1 m/h, gas injection showed no effect and an increase in critical flux was observed when increasing the V_L to 2 m/s. At the latter V_L, gas injection did show an important effect. Under all conditions tested, cake layer formation was again identified as the factor determining the critical flux. Figure 7.13(A) also presents the results of the critical flux determinations performed at high cross-flow velocities described in Chapter 5, using the sludge developed in the submerged MBR operated with acidified substrate (Figure 5.16C in Chapter 5). Critical fluxes measured in the VFA-CFMBR appear low when compared with those obtained with the sludge from the submerged MBR (VFA-SMBR). A lower particle size, induced by the high shear conditions, is the most likely explanation for the differences in filtration performances between sludges coming from VFA-SMBR and VFA-CFMBR. Figure 7.13(B) presents the cumulative particle size distribution of both sludges, measured when performing the critical flux determinations. Sludge from the VFA-CFMBR shows a lower particle size, however the difference seems small. Nevertheless, volume distributions tend to mask changes in the small particle size range, and the smallest particles in a poly-dispersed suspension can determine the filtration rate (Kim et al., 2002b; Kromkamp et al., 2002). Therefore we consider particle size as the most likely reason for the differences in critical fluxes observed in Figure 7.13(A).

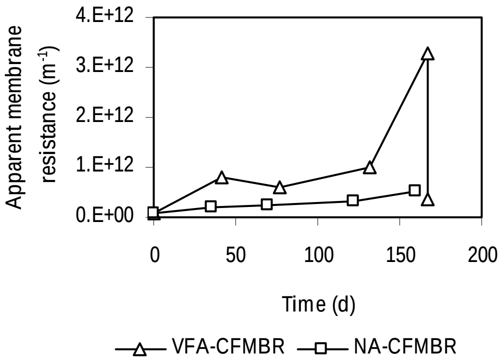

Figure 7.12. Apparent membrane resistance during the operation of the CFMBRs. Reduction of apparent membrane resistance for the VFA-CFMBR on day 167 is the result of the physical cleaning of the membrane.

Data from Figure 7.13 reveal what can be defined as “the shear rate dilemma”: since cake formation limits the attainable fluxes, an increase in shear should improve filtration performance. However, the high shear rate also reduces particle size, increasing the chances of particle deposition. Since it is not possible to achieve high surface membrane shear without exposing the sludge to high shear forces, the magnitude of the applied shear rate should be carefully determined, based on the properties of the studied system.

If the permeate flux achieved during the operation of the VFA-CFMBR is considered, costs related with energy and membrane requirements are decisive in the application of thermophilic anaerobic MBR technology. Figure 7.14 presents an estimation of the costs due to liquid recirculation and membrane acquisition/replacement. The costs have been determined based in the following assumptions: V_L 1.5 m/s, recirculation pump efficiency 60%, tubular membrane diameter 6 mm, total membrane length per pass 16 m, sludge viscosity 0.01 Pa·s, sludge density 1.05 g/L, TMP 0.5 bar. Energy requirements have been evaluated considering the sum of the required TMP and the pressure drop along the membrane. The latter value has been computed calculating the energy losses due to friction in the membrane tubes, applying a factor of 1.5 to account for other frictional losses, such as pipes, fittings, etc. Membrane lifetime and costs have been considered to be 5 years and 125 €/m²[*], respectively. Under these conditions, the costs of energy are higher than the costs of membrane acquisition/replacement. At the end of the experimental operation of the VFA-CFMBR, the attained flux was about 25 L/m²·h. If this flux is considered, energy and membrane related costs would be 0.30 €/m³ of permeate.

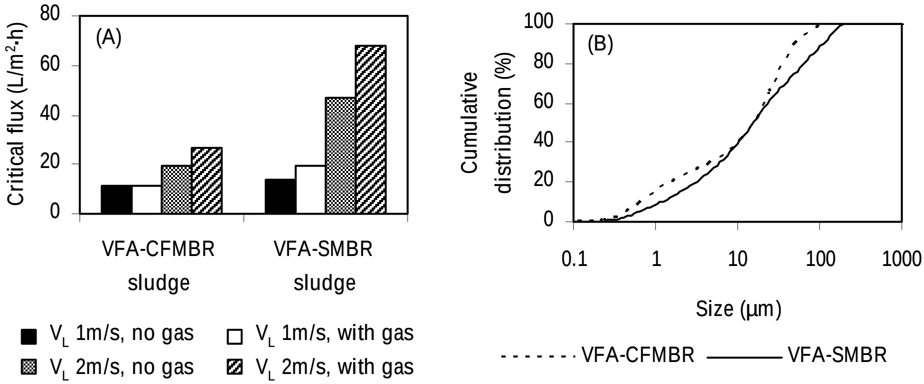

Figure 7.13. (A) Critical flux for the VFA-CFMBR, measured at two values of V_L, in presence and absence of gas injection. TSS was 28 g/L. Critical flux values for the sludge from the VFA-SMBR are presented for comparison (data from Chapter 5). Latter measurements were performed at a TSS of 30 g/L. (B) Cumulative particle size distribution of sludge from the VFA-CFMBR and VFA-SMBR, at the moment of the critical flux measurements.

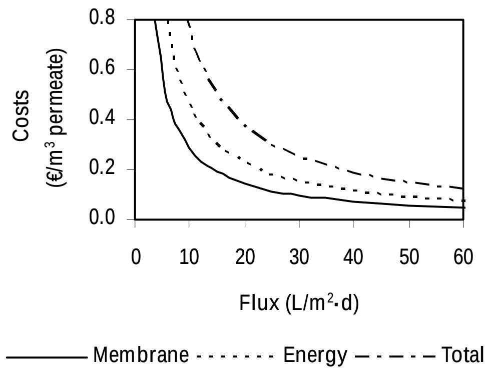

Figure 7.14. Costs associated with energy requirement due to liquid recirculation and membrane acquisition/replacement for a thermophilic CFMBR. See text for assumptions.

[*] Norit, personal communication (2007)

Figure 7.15 presents the critical flux determinations performed at the end of the NA-CFMBR operation. The observed critical flux values were lower than those for the VFA-CFMBR, i.e. not exceeding 10 L/m^2·h. Gas injection showed no effect, and the increase in V_L from 1 to 2 m/s produced only a marginal improvement in the critical flux.

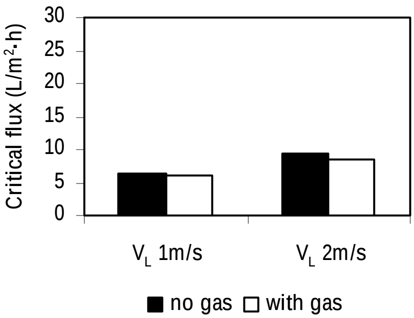

Figure 7.15. Critical flux of the NA-CFMBR, measured at two different liquid cross-flow velocities, in presence and absence of gas injection. TSS concentration was 28 g/L.

In order to determine if the development of acidogenic biomass was responsible for these poor filtration performances, a sludge sample of NA-CFMBR was separated in two fractions by centrifugation, following a similar procedure as the one described in Chapter 5. However, a longer period of centrifugation, i.e. 45 minutes, was applied this time. The sample was collected just after the final critical flux measurements, so solids concentration was 28 g TSS/L. Two fractions were separated, namely the pellet and the supernatant. The pellet was re-suspended to the original sample volume using the reactor permeate. Each fraction contributed with about 50% to the TSS of the reactor sludge. Therefore, critical flux assessment of the segregated fractions (pellet sludge and the supernatant sludge) were performed at a similar TSS concentration, i.e. about 14 g TSS/L. The membrane module was disconnected from the reactor, and critical flux was measured using each fraction, at a V_L of 1 m/s. Results are presented in Figure 7.16. The behaviour of the original sludge sample from the NA-CFMBR is also presented for comparison. Critical flux values as well as supra-critical TMP increase rates are presented. For better comparison, supra-critical TMP increase rates are expressed against the difference between the applied flux and the critical flux (J-J_C). The observed differences between the separated fractions are evident, for both critical flux and supra-critical TMP increase. Surprisingly, the behaviour of the supernatant coincides with the one of the original sludge sample, even though the solids concentration is much lower. This indicates that the supernatant fraction is fully determining the behaviour of the NA-CFMBR sludge. Mostly reversible cake layer formation was identified as the factor determining the critical flux, since resistance was easily reduced by the application of back-flush cycles.

The supernatant presented a very low acetotrophic methanogenic activity, only 0.25 g COD/g VSS·d. The hydrogenothrophic methanogenic activity was higher, i.e. 0.80 g COD/g VSS·d. Acetogenic activity from butyrate was also detected in the supernatant sludge, at a rate of around 1.0 g COD/g VSS·d. Acidogenic activities were 2.0 g COD/g VSS·d for gelatine and 2.6 g COD/g VSS·d for starch, indicating that it was composed at a high extent by acidogenic bacteria.

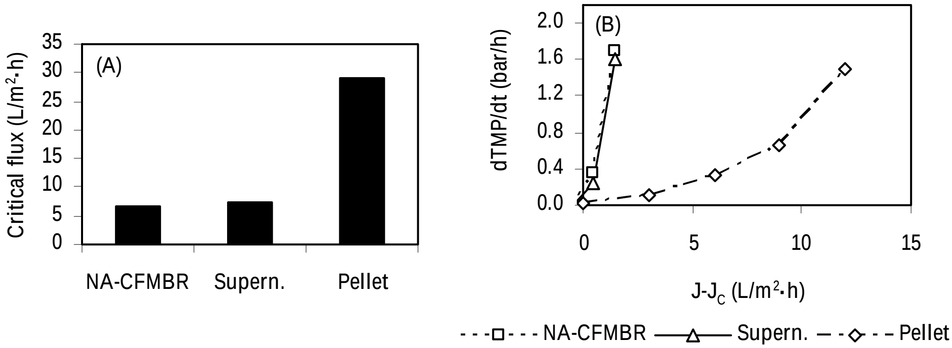

Figure 7.16. Critical flux (A) and supra-critical TMP increase rates (B) of the sludge from the NA-CFMBR and its fractions separated by centrifugation. A V_L of 1 m/s was used. TSS concentrations: 28 g/L for the NA-CFMBR sludge and 14 g/L for each of the fractions.

The supernatant fraction apparently also determined the rheology of the sludge, as can be seen in Figure 7.17. NA-CFMBR sludge presented a rheological behaviour similar to that of the supernatant fraction, despite the differences in TSS. The apparent viscosity of the pellet fraction was much smaller, in the entire range of shear stresses tested. The rheological behaviour of the soluble content of the NA-CFMBR sludge is also presented, in order to determine if the high apparent viscosity was related to the high concentration of SMP. The soluble content of the NA-CFMBR was separated by filtration using 0.45 µm membrane filters. Results indicate that the SMP indeed contributed to the sludge high apparent viscosity. This means that the sludge rheology from the NA-CFMBR is determined by both the soluble fraction and the solids contained in the supernatant fraction.

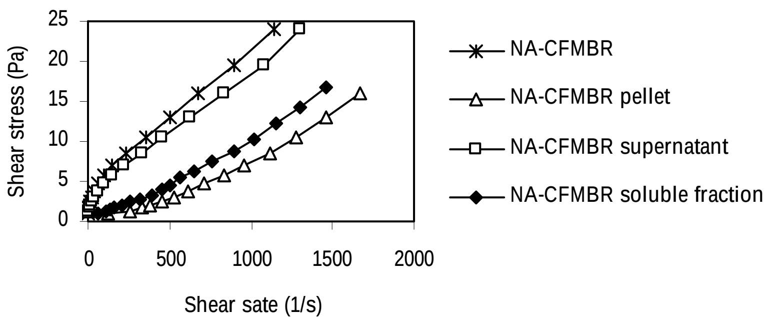

Figure 7.17. Rheological behaviour of the sludge from the NA-MBR, its centrifugation-separated fractions and soluble content. Solids concentrations were 28 g TSS/L for the NA-CFMBR, and 14 g TSS/L for the supernatant and pellet fractions.

The supernatant fraction of the NA-CFMBR also presented smaller particles than the pellet fraction, as expected, as can be seen in Figure 7.18. The combination of smaller particle sizes and the rheological behaviour of supernatant fraction are most likely playing a predominant role in determined its low filtration performance, which in turn determined the whole reactor behaviour.

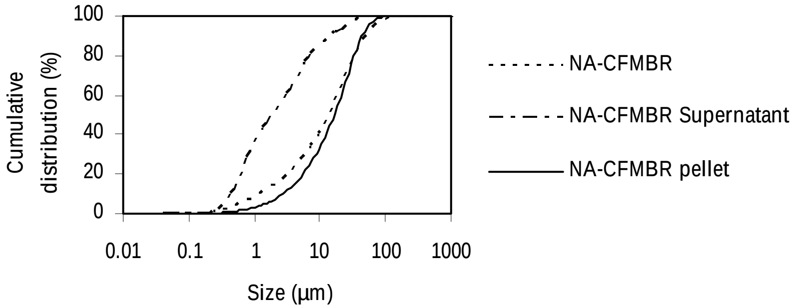

Figure 7.18. Cumulative particle size distribution of the sludge contained in the NA-CFMBR, and its fractions separated by centrifugation.

Figure 7.19 presents light microscopy pictures from the sludge of the VFA-CFMBR and the NA-CFMBR sludge fractions separated by centrifugation. The NA-CFMBR-supernatant shows abundant rod shape microorganisms. Observation under epifluorescence microscopy showed little fluorescence at 420 nm, confirming the low presence of methanogenic bacteria. Considering the values of SMA and SAA already commented, it is inferred that these microorganisms are acidogenic bacteria. Almost no flocs can be observed, which most likely is the reason for the low particle sizes presented in Figure 7.18. Images for the NA-CFMBR-pellet sludge and VFA-CFMBR sludge look surprisingly similar. Likely most of the acetotrophic methanogenic bacteria and an important fraction of the acetogenic bacteria are contained in the pellet fraction. This assumption is supported by the results of the SMA of the NA-CFMBR sludge and the SMA and SAA of the supernatant fraction.

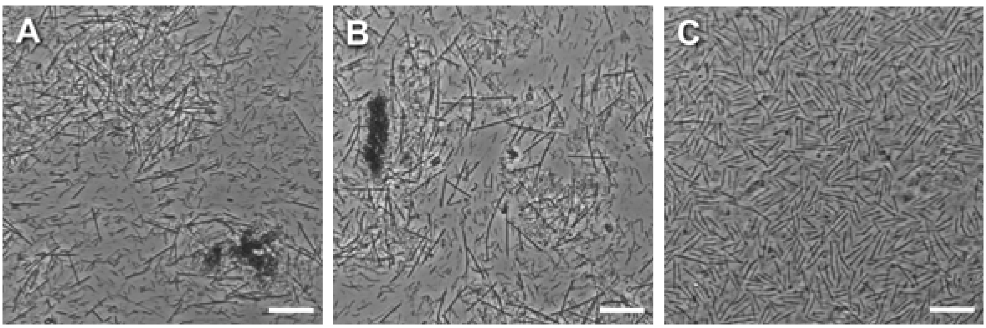

Figure 7.19. Light microscopy pictures from the sludge from the MBRs. (A) VFA-CFMBR; (B) NA-CFMBR centrifugation pellet; (C) NA-CFMBR centrifugation supernatant. Bar indicates 20 µm.

7.4. CONCLUSIONS

Cake formation is the main factor determining the applicable fluxes in anaerobic CFMBRs, irrespective of the substrate degree of acidification, and the amount of SMP retained inside the reactor. Membranes are subjected to very low levels of irreversible fouling, even when high concentrations of SMP are present (several grams per litre). This means that long term operation is possible in absence of chemical cleaning. However, changes in sludge properties due to the cross-flow operation, most likely particle size, were identified as a negative factor affecting the applicable flux.

When operating with an acidified substrate, final operational flux was about 25 $L/m^2 \cdot h$, at V_L 1.5 m/s, V_G 0.1 m/s and 24 g TSS/L. These operational conditions can be translated to an estimated cost based on membrane and energy requirements of about 0.30 €/m^3 of permeate.

A lower degree of substrate acidification resulted in important changes in sludge physical properties, in comparison with a sludge grown with fully acidified substrate. Sludge rheology and particle size showed significant changes. The latter physical properties are most likely responsible for the low fluxes attained in the NA-CFMBR at V_L values as high as 2 m/s.

Propionate oxidation showed to be the limiting step for the applied OLR in both CFMBRs. However, the observed propionate oxidation rates are in the same range of reported values for non-membrane based reactors such as UASB systems. Apparently, the shear forces applied in the CFMBRs did not impact the syntrophic conversions rates detrimentally.

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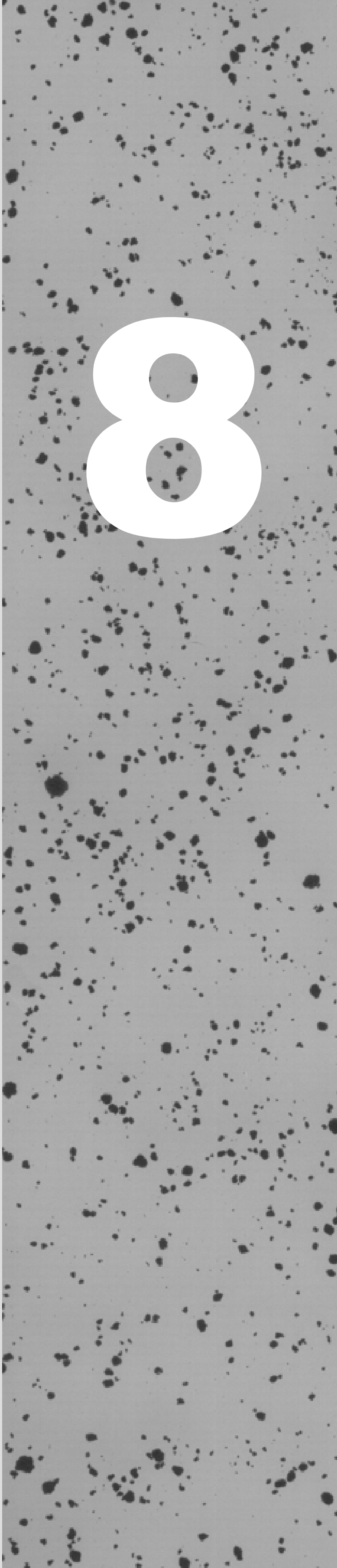

Application of membrane enhanced biomass retention to the anaerobic treatment of acidified wastewaters under extreme saline conditions

Abstract

Two sludge bed anaerobic reactors were operated for the treatment of an saline, completely acidified synthetic wastewater. One of the reactors was equipped with a microfiltration membrane, in order to achieve complete biomass retention. Reactors were operated at increasing organic loading rates and salinity. At a sodium concentration of 24 g/L propionate accumulation was severe. When salinity was reduced to 16 g/L, propionate oxidation in the membrane based reactor recovered after 40 days. This was not the case for the sludge bed reactor, in which propionate oxidation rates remained very low. This shows that the enhanced biomass retention achieved by membrane filtration can have a positive effect in retaining active halotolerant bacteria. Fluxes in the range of 10 to 15 $L/m^2 \cdot h$ were achieved during the membrane bioreactor operation, even though membrane was exposed to a solid concentration below 2 g/L. However, flux showed to be limited by cake formation and low levels of internal pore fouling were detected.

8.1. INTRODUCTION

Anaerobic treatment is considered the most cost-effective technology for organic matter removal from different kinds of wastewaters. The success of anaerobic treatment is attributed to its low operation and maintenance costs and the extreme high loading potentials that are brought about by biomass immobilization. However, anaerobic treatment of saline wastewaters may be hindered by the presence of sodium and other cations that cause inhibition of methanogenic bacteria. Saline effluents are produced during several production processes, such as fish and sea-food processing, chemical industries and tanneries.

Few studies have been performed about the application of anaerobic treatment for the removal of organic pollutants in highly saline wastewaters (Lefebvre and Moletta, 2006). Most of the available studies have been performed in the treatment of sea-food processing effluents (Boardman et al., 1995; Mendez et al., 1995; Omil et al., 1995; Aspe et al., 1997; Vidal et al., 1997).

Different levels of saline tolerance of anaerobic bacteria have been reported. Rinzema et al. (1988) found no acetoclastic methanogenic activities at sodium concentrations exceeding 16 g/L. The 50% activity inhibitory concentration (IC_{50}) was around 10 g/L, and no adaptation was observed after 12 weeks. A similar saline tolerance was observed by Liu and Boone (1991). Feijoo et al. (1995) analysed the sodium inhibition of different types of sludges. A higher tolerance was observed in those sludges coming from reactors treating highly saline wastewaters, which was interpreted as a consequence of sludge adaptation. IC_{50} values for acetoclastic methanogens of adapted sludge was 16.3 g Na^+/L, and 100% inhibition was observed at 21 g Na^+/L. Adaptation phenomenon to high salinity was also observed by Omil et al. (1995), during the operation of a pilot plant treating wastewater from a sea-food factory, over a two year period.

As discussed in Chapter 1, effluent turbidity seems to be a common problem during the treatment of high saline wastewaters. Membrane bioreactors (MBR) may represent an adequate solution for the problems of high effluent turbidity induced by extreme saline conditions. However, the use of membrane based biomass retention for the treatment of highly saline wastewaters has been barely analyzed. Reid et al. (2006) studied the effects of rapid changes in salinity on the physical and chemical properties of the sludge and its relation with membrane permeability, using a submerged aerobic MBR. Vallero et al. (2005) studied the sulfate reduction process at 50 g NaCl/L, in an anaerobic membrane bioreactor (AnMBR), inoculated with a pure culture of *Desulfobacter halotolerans*. To our knowledge no reports are available about the application of AnMBRs for the removal of organic matter from saline wastewaters. Such a system may provide conditions favourable to the retention and development of halotolerant and/or halophilic anaerobic microorganisms, and at the same time provide a treated wastewater free of suspended solids.

The present research studies the application of membrane based biomass retention to the anaerobic treatment of acidified wastewaters under highly saline conditions. Two granular sludge bed reactors were operated at extreme salinity: one of them was equipped with a membrane microfiltration module to ensure total biomass retention. The performance of both reactors was comparatively studied through 310 days of operation. The effect of membrane assisted biomass retention is analyzed and discussed.

8.2. Materials and methods

8.2.1. Reactors setup

Two anaerobic reactors were used to conduct this study: an upflow anaerobic sludge bed (UASB) reactor and an AnMBR. Reactors were 5 L of useful volume. Schematic representations of both reactors are presented in Figure 8.1. The AnMBR consisted of a sludge bed reactor with a three phase separator on top, like the UASB reactor, connected to a membrane module. A single polymeric inside/out microfiltration tubular membrane was used, with a nominal pore size of 0.2 µm. Membrane tube dimensions were 1.4 cm diameter and 50 cm long and the membrane area was 0.022 m^2. The membrane module was operated with gas sparging inside the membrane tube. Biogas was recirculated for this purpose. Glass tubes of the same internal diameter as the membrane were attached to each side of the membrane tube, to visually observe the gas/liquid flow pattern. The membrane module was operated with a liquid recirculation, driven by the gas-lift effect. The reactor was connected to the membrane module via the reactor recirculation. This provided a continuous flow of liquid from the reactor to the membrane module and vice-versa. Since most of the granular sludge was retained in the reactor, the membrane was only exposed to the suspended sludge. For the purpose of this paper, the term suspended sludge refers to that fraction of biomass that, due to its low particle size, is rinsed from the sludge bed and separator area in either of the reactors. In the case of the AnMBR, this sludge is retained in the system by the membrane. In the case of the UASB, this sludge can leave the reactor with the effluent. Permeate was collected from the membrane module by a peristaltic pump (Watson Marlow 323U, UK), which provided the required trans-membrane pressure (TMP). TMP was measured by a pressure sensor (AE Sensors ATM, The Netherlands) connected to the membrane module. The system was operated in such a way that the flow of permeate was higher than the reactor influent. Excess permeate was returned to the reactor through an overflowing vessel. Liquid recirculation was applied in both reactors in order to provide an ascending superficial liquid velocity in the range 0.5-0.7 m/h. Both reactors were operated at 30 °C.

8.2.2. Reactors operation

Both reactors were fed with a synthetic wastewater composed of a volatile fatty acids (VFA) mixture, containing acetate, propionate and butyrate in the same chemical oxygen demand (COD) proportions. Inlet COD concentration was 10-11 g/L. Salinity was provided by the addition of 4 cations: sodium, magnesium, potassium and calcium, in the same ratio as in sea water. Ratios were: Mg^{+2}/Na^{+}: 0.122, K^{+}/Na^{+}: 0.039, Ca^{+2}/Na^{+}: 0.037. All cations were provided as their chloride salts. Around 15% of the sodium was provided as NaOH, required for VFA neutralization. For simplicity, salinity is expressed as solely sodium concentration. Concentration of the other cations can be then easily evaluated using the ratios previously provided. Organic loading rate (OLR) was varied by changing the hydraulic retention time. Initial biomass concentration for both reactors was 30 g/L of volatile suspended solids (VSS). Reactors were inoculated with sludge coming from a full scale UASB reactor treating wastewater from a styrene and propene-oxide production plant of Shell, Moerdijk, The

Netherlands. The latter industrial wastewater contains a sodium concentration in the range 10- 15 g/L, with acetic and benzoic acids as main sources of COD.

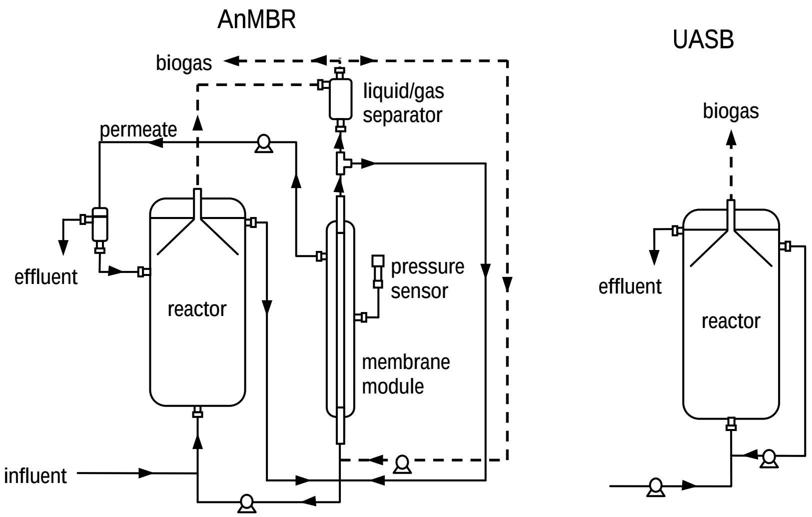

Figure 8.1: Schematic representation of the AnMBR and the UASB reactor setups. Doted lines indicate gas flows.

8.2.3. Analyses

Total suspended solids (TSS) and VSS were determined according to Standard Methods (APHA et al., 1998). COD was determined using Lange COD cuvette tests (Hach Lange, Germany). Samples were diluted in order to avoid interference from chloride ion on COD determinations, following COD tests manufacturer recommendations. Suspended sludge particle size distribution was measured by laser diffraction analysis (Coulter LS230, Beckman Coulter, USA). The latter particle size data are presented based on volume distributions. Granule size distribution was measured by image analysis according to Jeison and Chamy (1998), based on the individual observation of at least 2500 granules. Granules sizes are presented based on a number distribution. For granular sludge size distribution only particles over 0.15 mm were considered. VFA were determined in an Hewlett-Packard gas chromatograph (model 5890 series II) with a flame ionization detector (FID), equipped with a column AT Aquawax-DA (Alltech).

8.2.4. Granule strength

Granule strength was evaluated by fines generation in a gas sparging column (Pereboom, 1997). A 1.2 L useful volume column was used. Column dimensions were 5.6 cm diameter and 50 cm high. Tests were performed with 200 mL of settled sludge and a nitrogen gas flow rate of 0.9 L/min. The concentration of fines was measured every hour, for a period of 5 hours. Fines are defined as the particles below 100 µm. A sieving mesh was used to separate particles over 100 µm from the samples. The rate of fines generation in time, expressed as solids percentage of the original amount of sludge, is used to represent the granule strength.

8.2.5. Specific methanogenic activity and sodium response curves

The specific methanogenic activity (SMA) was determined in duplicates as described in Chapter 4. Biomass concentration was 1 g VSS/L, unless otherwise indicated. Different substrates were used: acetate, propionate, butyrate, hydrogen, or an acetate-propionate-butyrate mixture at a COD ratio of 1:1:1. For SMA determinations using hydrogen as substrate, serum bottles headspace was filled with a mixture of 80% hydrogen and 20% carbon dioxide, at an initial pressure of 1.6 bar. In the latter case, activity was determined following the decrease in pressure, due to hydrogen consumption.

Sodium response curves were performed by measuring the SMA at different sodium concentrations. Inoculum characterization was performed measuring SMA with the VFA mixture as substrate at the following sodium concentrations: 0, 10, 15, 20, 25, 30 g/L. Only sodium chloride was added as source of salinity during the latter determinations.

At the end of the reactors operation, sodium response curves were performed with acetate, butyrate, propionate and hydrogen as substrates, independently. In the latter case, sodium together with magnesium, potassium and calcium were added, in the same proportion than for reactors operation. SMA determinations were performed with samples of granular and suspended sludge coming from both reactors. Suspended sludge samples were previously concentrated by centrifugation. Due to the low concentration of suspended sludge samples, activities could only be performed at a VSS concentration of 0.5 g/L. Sodium concentrations tested were 0, 8, 16, 24 and 32 g/L.

All SMA determinations were performed with two substrate feedings, in order to ensure biomass acclimatization to the conditions of each assay. Second feeding was performed once substrate from the first one had been depleted. Reported SMA results presented correspond to the second substrate feeding. IC_{50} values were evaluated considering the maximum observed activity as 100%. SMA determinations were performed at a temperature of 30 °C.

8.2.6. Apparent membrane resistance

Apparent membrane resistance was determined following the procedure already described in Chapter 2. For this purpose, the membrane module was disconnected from the reactor, rinsed and filled with demineralised water.

8.2.7. Membrane observation with scanning electron microscope

Membrane samples were taken to be observed under the scanning electron microscope (SEM). Samples were collected by cutting a small piece from the end of the membrane tube. Samples were fixed, dried and observed as described in Chapter 4.

8.2.8. Physical and chemical membrane cleaning

Two types of membrane cleaning procedures were used to reduce filtration resistance during the operation of the AnMBR: chemical and physical cleaning. Chemical cleaning was performed as described in Chapter 4. The membrane was chemically cleaned in the same membrane module, after disconnection from the reactor. Physical cleaning consisted of the physical removal of the cake layer from the membrane, using a soft wool brush to gently scour the inner surface of the membrane tube.

8.3. RESULTS AND DISCUSSION

8.3.1. Inoculum characterization

Figure 8.2 presents the sodium response curve for the inoculum sludge, using a VFA mixture as substrate. Only sodium was used in this determination (no magnesium, potassium or calcium). SMA values are low, if compared with typical ones from methanogenic sludge grown under non-saline conditions. Interestingly, Figure 8.2 shows that IC_{50} is over 20 g/L (0.87 M), and that an important level of activity is still present at a sodium concentration of 30 g/L (1.3 M). This remarkable sludge tolerance to sodium is certainly the result of prolonged exposure to high saline conditions, which enhanced either the adaptation of microorganisms, or the selection of those presenting a higher saline tolerance. Granules were extremely small and weak. Average particle size was only 0.31 mm, and almost no granules over 1 mm diameter were present (less than 1 %).

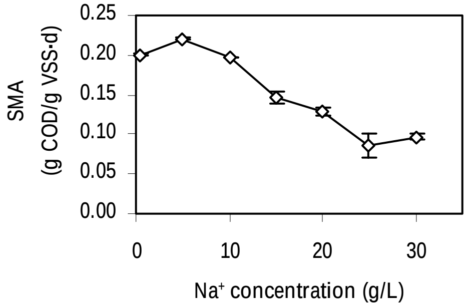

Figure 8.2: Sodium response curve for the reactors inoculum, using a VFA mixture as substrate. Only sodium chloride was used as source of salinity. Error bars represent the standard deviation between duplicates.

8.3.2. Reactors operation

Figure 8.3 presents the applied OLR and sodium concentration during the operation of the UASB reactor and the AnMBR. Both reactors were operated under the same conditions. During the first 100 days, OLR and salinity were increased in steps, up to 12 g COD/L·d and 24 g Na^+/L, respectively. Considering the initial reactors biomass concentration, the maximum applied volumetric loading of 12 g COD/L·d, corresponds to a sludge load of 0.4 g

COD/g VSS·d. A sodium concentration of 24 g/L (1.04 M) corresponds to 1.7 times sea water concentration. As described in materials and methods, magnesium, potassium and calcium were also supplied, which means that at 24 g Na^+/L, the total cations concentration was 1.2 M, 87% corresponding to sodium. At 24 g Na^+/L, chloride concentration was 46 g/L (1.3 M). During the first 95 days of operation, low effluent VFA concentrations were measured, as can be seen in Figure 8.4. Interestingly, during this period, the UASB reactor presented lower effluent VFA concentrations than the AnMBR. This difference is probably related with AnMBR unstable operation due to membrane maintenance. As will be discussed later, reactor was stopped in several occasions for measuring the membrane resistance and to perform cleaning operations.

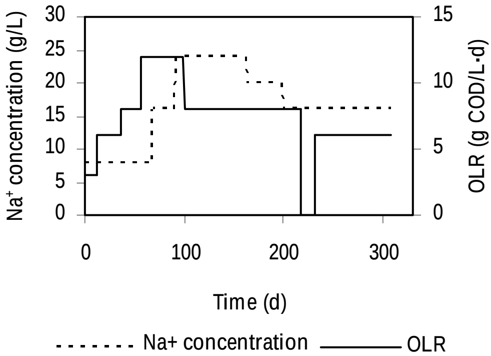

Figure 8.3: Applied OLR and influent sodium concentration during the operation of the AnMBR and the UASB reactor. Potassium, magnesium and calcium were also added, providing the same ratio with sodium as in sea water.

After increasing sodium concentration to 24 g/L, VFA concentration in both reactors reached over 4 g COD/L. OLR was then decreased to 8 g COD/L·d, keeping the sodium concentration at 24 g/L. A rapid decrease in VFA concentration was observed in response to the OLR reduction. However, VFA remained over 1 g COD/L, and tend to increase during the following 100 days of operation. Sodium concentration was decreased to 20 and then to 16 g/L, on days 160 and 200, respectively. However, VFA concentration remained in the range 2-3 g COD/L. Interestingly, most of the measured VFA in the effluent of both reactors was propionate. Figure 8.4 also presents the contribution of propionate to the total VFA. Concentrations were expressed as COD to evaluate this percentage. From Figure 8.4 it is clear that propionate oxidation is the limiting step for VFA degradation under high saline conditions. Effluent acetate and butyrate concentrations remained low during reactors operation, most of the time below 200 mg COD/L, even during the operation at 24 g Na^+/L. Gebauer (2004) also identified propionate oxidation as the limiting step during the anaerobic degradation of sludge from saline fish farm effluents, working with a sodium concentration close to 10 g/L. Additionally, Feijoo et al. (1995) measured an IC_{50} for propionate that was 40% lower than for acetate, when working with a saline adapted anaerobic sludge.

Since the reduction in salinity to 16 g Na^+/L did not produce a decrease in propionate concentration, it is inferred that the extreme salinity of 24 g Na^+/L had exerted an irreversible toxic effect. For comparison, between days 70 and 90 reactors were already operated at 16 g Na^+/L, at an even higher OLR, with good VFA removals. On day 217 reactors feeding was stopped, to enable a reduction in the VFA concentration. On day 231 reactors feeding was resumed, but at an OLR of 6 g COD/L·d, a value that was kept until the end of the operation. During the last 70 days of operation, the AnMBR showed a slow recovery, achieving an effluent VFA concentration equivalent to 600 mg COD/L, towards the end of the operation. On the other hand, UASB effluent concentrations rapidly returned to the range 3-3.5 g COD/L, being propionate the main responsible for this high VFA concentration.

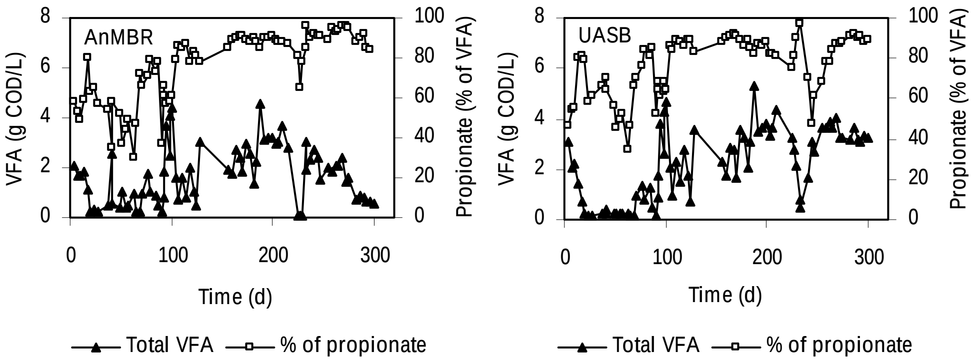

Figure 8.4: Effluent VFA concentration and propionate contribution to total VFA (in terms of COD) during the operation of the AnMBR and the UASB reactor.

Figure 8.5 presents the effluent COD concentration during the operation of both reactors. The COD concentration correlates well with the VFA concentration, which shows that effluent COD was composed mostly by non-converted VFA. Permeate COD and reactor soluble COD were almost coincident, as can be seen in Figure 8.5, showing that no accumulation of soluble COD occurred in the AnMBR.

By the end of the operation, the amount of biomass contained in each reactor was 128 and 195 g VSS in the UASB and in the AnMBR respectively. This represents 85 and 130% of the initial sludge amount. Biomass washout was observed in the UASB especially during the first 100 days. During that period, solids in the UASB reactor effluent were in the range 0.2-0.4 g TSS/L (0.15-0.3 g VSS/L). After day 100, effluent solids decreased to around 0.1 g TSS/L (0.07 g VSS/L). This was likely the result of the decreases in OLR and COD removal, which produced a reduction in the biogas production, and therefore a decrease in the reactor turbulence. An increase in the reactor VSS concentration was observed in the AnMBR, which provided complete biomass retention. Interestingly, most of the biomass in the AnMBR, close to 97%, remained in the sludge bed. By the end of the operation, suspended sludge concentration was barely 1 g VSS/L. Low suspended sludge concentration in the AnMBR was most likely the result of low biomass growth, and low abrasion forces and turbulence that reduced fines formation.

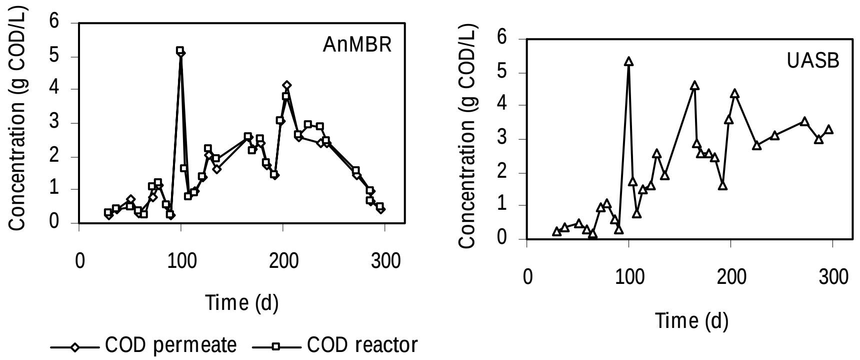

Figure 8.5: Soluble COD concentration during the operation of the AnMBR and the UASB reactor. In the case of AnMBR, COD concentrations in the permeate and in the reactor are presented. In the case of UASB, effluent concentration is presented.

Granule size distribution in both reactors experienced no big changes, compared with the inoculum sludge, as can be seen in Figure 8.6. Granules remained very small, maintaining an average close to 0.3 mm, like the inoculum. No change in granule size suggests no preferential washout of smaller particles in the UASB. This is most likely the result of a narrow distribution in particle size.

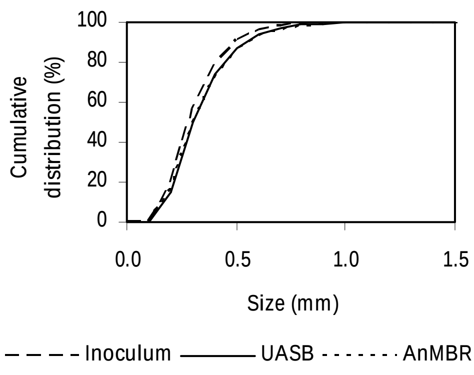

Figure 8.6: Cumulative granule size distribution of the inoculum sludge and the sludge from the reactors at the end of their operation.

Granular sludge used in this study showed to be extremely week. Abrasion experiments were performed in a bubble column to measure the granule strength of the inoculum, and the sludge from each reactor. Sludge from a full scale UASB reactor treating recycled paper wastewater (Industriewater Eerbeek, Eerbeek, The Netherlands) was also analysed for comparison. No significant changes in granule strength were observed during AnMBR or UASB operations. However, sludge from both reactors showed a granule strength more than 5 times lower than the Eerbeek sludge. During the present research granule strength and size were high enough to allow UASB reactor operation. However, an important level of sludge washout was observed, even though hydraulically induced shear rate in lab scale reactors is usually low. In full scale reactors, abrasion forces and turbulence are much higher, factors that may put at risk the required biomass retention, when working at high saline conditions.

8.3.3. AnMBR filtration performance

Figure 8.7 presents the filtration resistance during the operation of the AnMBR. During the first 50 days, flux was gradually increased until 15 L/m^2·h. Increasing filtration resistances were measured during the first 100 days of operation. Gas superficial velocity (V_G) inside the membrane tube was gradually increased during the first 100 days from 100 to 400 m/h, as an attempt to control membrane fouling. From day 100 until the end of the operation, V_G was kept at 400-450 m/h. The latter V_G was enough to generate a gas slug flow regime within the membrane. Further increases in V_G did not enhanced membrane filtration.

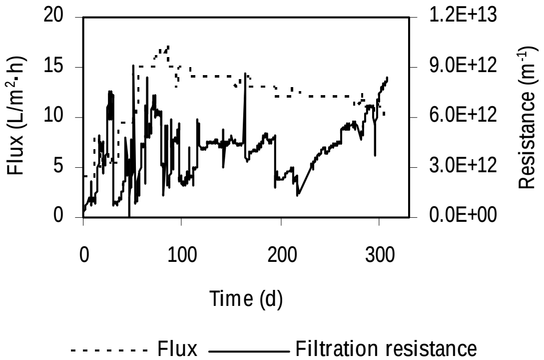

Figure 8.7: Applied permeate flux and filtration resistance during the continuous operation of the AnMBR.

Apparent membrane resistance increased fast during the first 100 days of operation, as can be seen in Figure 8.8. The membrane was chemically cleaned on 3 occasions during this period, in order to reduce the resistance, and the resulting TMP. On day 85 a physical cleaning procedure was performed, instead of a chemical cleaning. Cleaning efficiency was as high as the chemical cleanings previously performed (Figure 8.8). This is clear when observing Figure 8.9, which presents a SEM picture of the membrane surface just after the physical cleaning procedure performed on day 85. Membrane surface appears almost completely free of deposited material, and no superficial pore blocking or pore narrowing is observed. Between days 100 and 300 apparent membrane resistance remained below $3.1 \cdot 10^{12}$ m^{-1}, thanks to the increase in V_G, the decrease in flux and the physical cleaning performed on day 195. From day 100 onwards, filtration resistance (Figure

8.7) exceeded the latter value, indicating a reversible cake layer formation within filtration cycles. A final physical cleaning was performed at the end of the operation, which yielded an apparent membrane resistance of $1.5 \cdot 10^{12}$ m^{-1}. This value is considered interestingly low, after more than 200 days of operation in absence of chemical cleaning.

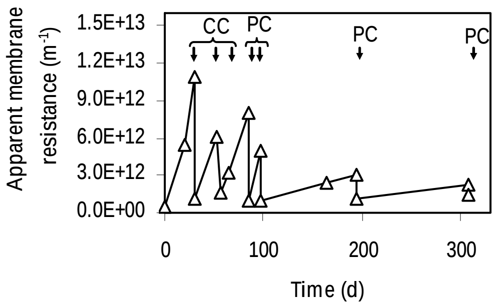

Figure 8.8: Apparent membrane resistance during the continuous operation of the AnMBR. Arrows indicate when chemical cleaning (CC) and physical cleaning (PC) operations were performed.

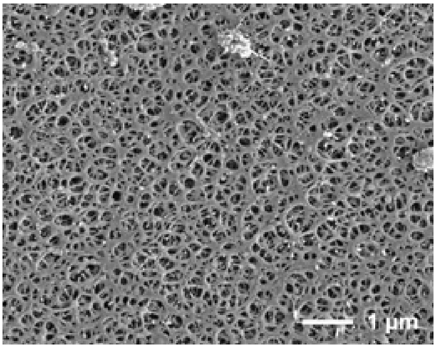

Figure 8.9: SEM picture of membrane surface after the first physical cleaning procedure, performed on day 85.

The high effectiveness of physical cleaning procedure indicates the occurrence of low levels of internal pore fouling. Cake formation is then the main factor limiting the applicable flux. This agrees with results presented in Chapter 4, that showed that in submerged AnMBRs cake formation is the limiting factor for the applied flux, and that cake consolidation is the main phenomena contributing to the increase of the apparent membrane resistance. Operational flux could not exceed 15 $L/m^2 \cdot h$, even though suspended sludge concentration in the AnMBR was below 2 g TSS/L. Since cake formation is likely determining the flux, higher surface shear rates may be applied in order to increase the operational flux.

8.3.4. Sodium response curves

Figure 8.10 presents the sodium response curves performed with suspended and granular sludge from each reactor, performed at the end of the UASB and the AnMBR operation. The AnMBR sludge showed higher activities than the sludge from the UASB reactor. Furthermore, suspended sludge presented an activity several times higher than that of the granular sludge, especially in the case of the AnMBR. This may be explained by a lower fraction of active biomass in the granular sludge. Furthermore, apparent activity in granules may be affected by mass transfer limitations. Indeed, in anaerobic granules usually only the outer layer is active (Alphenaar et al., 1993).

Propionate oxidation is by far the slowest process, as was also observed during the operation of the reactors. Acetoclastic and hydrogenotrophic methanogenic activities presented high values, even at elevated salinity levels. The IC_{50} value for acetate conversion was around 25 g Na^+/L for the granular and suspended sludges of the AnMBR. IC_{50} value for hydrogenotrophic methanogens in the AnMBR was below 20 g Na^+/L, for both granular and suspended sludge. Methanogenic bacteria from the UASB reactor presented similar IC_{50} values. Feijoo (1995) suggested a higher sensitivity of acetotrophic methanogens to sodium, in comparison to hydrogenotrophic methanogens. However their observation was based on experiments performed with a non adapted sludge to highly saline conditions, which is most likely the reason for the discrepancy in results.

By multiplying the maximum methanogenic activity with the biomass concentration, the theoretical maximum reactor capacity can be estimated. The maximum reactor capacities of the AnMBR at 16 g Na^+/L, for acetate, propionate, butyrate and hydrogen were 17, 1.5, 15 and 3 g COD/L·d, respectively. Maximum reactor capacities for the UASB reactor at 16 g Na^+/L were 6.9, 0.4, 6.7 and 1.7 COD/L·d, respectively; 2 to 3 times lower than those for the AnMBR. OLR towards the end of the operation was 6 g COD/L·d, which means that the applied load of each VFA was 2 g COD/L·d. Therefore, acetate and butyrate loads were far below the maximum capacity of both reactors to degrade those VFA. On the contrary, reactors maximum capacities for propionate degradation were only 25% and 75% of the actual applied load for the UASB and the AnMBR, respectively. These values agree well with the propionate removal at the end of the reactors operation: 15-20% and 85%, respectively.

Due to unfavourable thermodynamics for the degradation of propionate, low hydrogen partial pressure is required, which is accomplished by an efficient interspecies transfer of hydrogen form the hydrogen producing bacteria, to the hydrogen utilizing methanogens (Stams, 1994). During anaerobic oxidation of VFA, three and two moles of hydrogen are stoichiometrically produced per mol of converted propionate and butyrate, respectively. If all butyrate and propionate contained in the reactors influent is oxidized, at an OLR of 6 g COD/L·d, acetogenic reactions should produce 0.079 mol of hydrogen per litre of reactor per day. This means that an hydrogenotrophic methanogenic capacity of at least 1.3 g COD/L·d is required. This calculation assumes that acetate is oxidized by acetoclastic methanogenesis only. As already mentioned, maximum reactor capacities for hydrogen at the end of reactors operation, at 16 g Na^+/L, were 3 and 1.7 g COD/L·d for the AnMBR and UASB, respectively. Required and maximum available hydrogenotrophic methanogenic capacities are similar in the case of the UASB, which suggests that the prevailing hydrogenotrophic capacity might be limiting propionate oxidation. However, it must be considered that hydrogenotrophic methanogenic activity may be underestimated due to mass transfer restrictions during the SMA measurement, since hydrogen must be transferred from the gas to the liquid phase, and then diffuse inside the flocs or granules.

Local concentration gradients and transfer fluxes are of importance for hydrogen interspecies transfer. This is the reason why optimum conditions for this transfer are usually present in biofilms due to lower distance between syntrophic bacteria (Schmidt and Ahring, 1996). Strikingly, propionate oxidizing specific activities of suspended sludges were higher than those of granular sludges. This might be, however, the result of the presence of small syntrophic conglomerates in the suspended sludge, the limitation of hydrogen mass transfer into the granules, or the large abundance of hydrogentrophic methanogens in the suspended sludge that compensates the increased distances between hydrogen producers and hydrogen consumers. In addition, a low fraction of active biomass in the granular sludge may also contribute to the observed relatively low level of propionate oxidation rate. Further research is needed to clearly determine the effect of high saline conditions on propionate oxidation in anaerobic digestion.

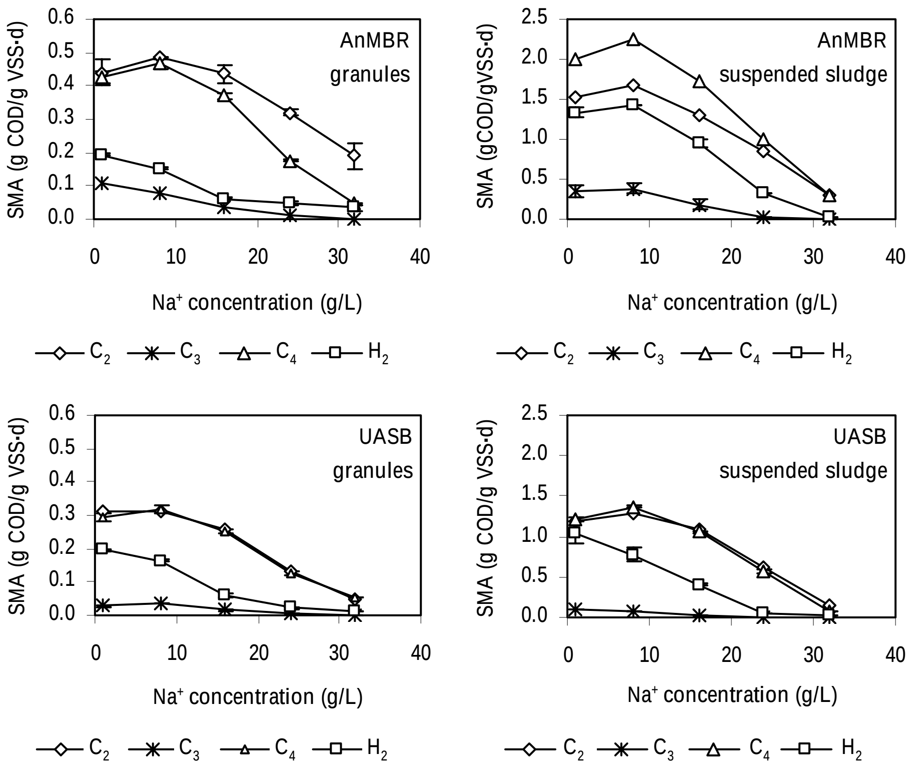

Figure 8.10: Sodium response curves for granules and suspended sludge from UASB reactor and AnMBR. SMA was measured individually with acetate (C_2), propionate (C_3), butyrate (C_4) and hydrogen (H_2) as substrates. Sludge samples for SMA analysis were taken at the end of rectors operation. Error bars represent the standard deviation between duplicates.

The effect of the membrane assisted enhanced biomass retention to the capacity of the AnMBR can be estimated, evaluating the conversion capacity of the suspended sludge. At 16 g Na^+/L, suspended sludge of the AnMBR accounted for 5, 8, 7 and 18% of the reactors overall maximum capacity for acetate, propionate, butyrate and hydrogen, respectively. Apparently, the contribution of the suspended sludge to overall performance is not particularly high. However, due to the low particle size distribution of the granular sludge present in the sludge bed, the membrane separation process apparently also determined the retention of small granules that otherwise would have washed out. This is supported by the observed reduction in biomass concentration in the UASB reactor. Higher SMA of AnMBR sludge also indicates that this reactor was more efficient in retaining active biomass.

8.4. Conclusions

The use of membrane based biomass retention for the treatment of highly saline acidified wastewaters showed to have a positive effect over the retention of active biomass, meaning higher loading potentials. AnSMBR sludge activity was significantly higher than that of the UASB reactor. Very small and week granules were observed in both reactors, which may negatively affect long term biomass retention in UASB reactors treating high saline wastewater. Long term continuous operation at high salinity levels resulted in superior levels of salt tolerance. The observed IC_{50} value for acetotrophic methanogenesis was about 25 g Na^+/L. However, anaerobic treatment of acidified wastewaters at extreme salinity may be restricted by the rate of propionate oxidation. Interspecies hydrogen transfer may be related to this behaviour. Membrane filtration in the AnMBR was fully determined by cake formation, and low levels of internal pore fouling were observed after 200 days of operation in absence of chemical cleaning.

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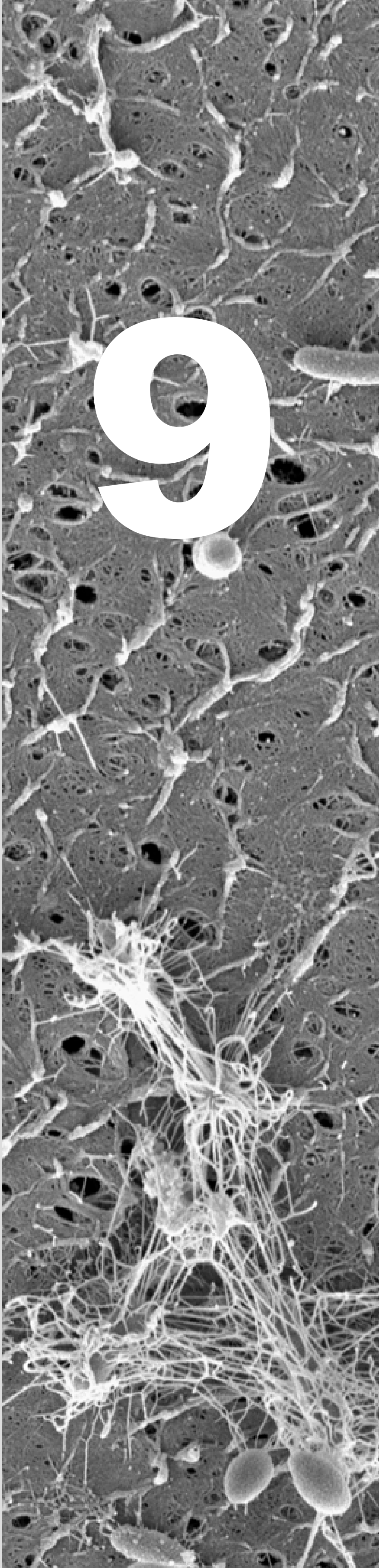
Summary and general discussion



9.1. Application of anaerobic membrane bioreactors

Biomass retention is a prerequisite feature for an efficient, successful and cost-effective application of anaerobic high-rate technology to wastewater treatment. Following the historic developments in anaerobic treatment, the formation of sludge flocs, biofilms or granules is the generally applied strategy to achieve this goal. Sludge granulation and biofilm formation is nowadays considered a simple and reliable way to ensure high sludge retention times at short hydraulic retention times, enabling reactor operation at high active biomass concentrations, and thus high conversion capacities.

At present, anaerobic high-rate technology is worldwide applied to a range of very different kinds of wastewaters, mostly coming from food processing industries (van Lier, 2007). These wastewaters are generally characterised as moderately concentrated, with a relatively high to high biodegradability. However, many wastewaters occur which have characteristics that limit the stable formation of microbial aggregates, e.g. wastewaters with high salt concentrations, extreme temperatures, chelating organic compounds, specific surfactants, etc. It is expected that the quantity of such types of extreme wastewaters will increase in the near future, owing to reduction in industrial water consumption and the general strategy towards industrial water loop closure. For such conditions, membrane enhanced biomass retention represents an alternative way to concentrate active biomass in anaerobic wastewater treatment systems. Even though it represents a highly efficient way for biomass retention, it inevitably involves higher operational and investment costs, compared to granular sludge based or biofilm based technologies. Obviously, membrane bioreactors (MBR) feasibility under anaerobic conditions will most likely be determined by the techno-economic benefits that the membrane enhanced biomass retention can provide. Anaerobic MBR systems could be of particular interest for the treatment of the above-mentioned extreme wastewaters that hamper satisfactory biofilm formation, while stable long term operation of granular sludge bed or biofilm based technologies treating such wastewaters is questionable. The treatment of wastewaters presenting high concentrations of organic solids could also greatly benefit from the total solids retention, since no solids wash-out from the reactor is possible. Other challenges include the accumulation of specific bacteria required for the conversion of recalcitrant and slowly biodegradable compounds and the combination of MBR technologies with other membrane post-treatment systems, avoiding the generally applied aerobic post-treatment step. Considering the ongoing trends in industries to reduce specific water consumption, and thereby drastically changing the process water characteristics, MBR application opportunities are expected to grow in the future.

Recognising the hydraulic limitations of an MBR set by the attainable membrane flux, it is obvious that highly concentrated wastewaters offer better perspectives for MBR application than low strength wastewaters. The wastewater organic matter concentration determines to a high extent the applied hydraulic retention time, which in turn defines the flow of permeate that has to be achieved. For a given flux, the latter value will determine the membrane requirements, influencing capital and operational costs. Therefore, even though the application of anaerobic MBR technology to low strength wastewaters may become technically feasible, its economical feasibility will be strongly determined by the prevailing membrane prices and the flux levels that can be achieved.

9.2. MICROBIAL ACTIVITY AND SYNTROPHIC RELATIONS

One of the potential disadvantages of MBRs is that they are usually based on CSTR systems with suspended active sludge, i.e. biomass present in the form of small flocs. Biofilms or granules have been recognised as an efficient way to enhance syntrophic interactions between microorganisms, since interspecies intermediates transfer is facilitated due to microorganisms proximity. Some authors have stated that high mixing conditions in CSTR systems may be detrimental for efficient anaerobic degradation of organic matter, since it would disrupt the spatial juxtaposition of syntrophic organisms (McMahon *et al.*, 2001; Kim *et al.*, 2002). Moreover, Brockmann and Seyfried (1997) even postulated that the observed lower specific conversion rates of sludge form an anaerobic MBR, resulted from the high shear forces at the membrane filtration device. However, during the present research no significant evidence was found indicating that operation with suspended sludge represented a serious draw-back for microbial activity. The negative impact of sludge dispersion is likely off-set by an efficient accumulation of highly active bacteria, while mass transfer resistance in the prevailing small particles is likely very low or even negligible. The attained sludge loading rate during the operation of a mesophilic submerged MBR (Chapter 4) was surprisingly high, while 85% of the sludge presented a particle size below 100 μm. Apparently, the small flocs are sufficient in size to provide suitable conditions for interspecies intermediates transfer. Moreover, when operating side-stream MBRs under high cross-flow liquid velocities (up to 1.5 m/s), no indication was found suggesting a negative effect of cross-flow on specific sludge activities (Chapter 7). SMA values were comparable with those reported containing biomass in the form of biofilm or granules. This means that anaerobic degradation of organic matter can indeed successfully proceed in MBR systems, without the need for granules or biofilms. The latter will most likely be true as long as the shear stress is kept at a certain level. For that purpose, during the operation of the side-stream MBRs presented in Chapter 7, the post-membrane back-pressure valve was eliminated and liquid cross-flow velocities up to 1.5 m/s were applied.

9.3. CAKE FORMATION: MAIN FACTOR LIMITING THE APPLICABLE FLUX

In the present thesis, research on the feasibility of anaerobic MBRs is described, applying different configurations, substrates and temperatures. Surprisingly, under all tested conditions cake formation showed to be the key factor limiting the applicable flux. This may be the result of the application of high biomass concentrations, exceeding concentrations of 20 g/L. Very low levels of irreversible pore fouling were observed, under all reactors operational conditions. This means that long term operation can be achieved in the absence of chemical cleaning. This is a finding of crucial importance, since chemical cleaning procedures affect reactor operation due to the need of membrane maintenance. Moreover, a low frequency of chemical cleaning procedures will likely result in a longer membrane lifetime. The latter is also of major importance, since membrane replacement represents one of the most important costs for MBR application.

Low pore fouling can be attributed to cake layer formation. If the membrane is covered by a cake layer, it is no longer exposed to the suspension, and pore blocking and other fouling mechanisms are less likely to occur. Cake formation also implies that the membrane material and exact pore size may not play a significant role in determining the flux. Once the membrane surface is covered by sludge, its properties do not play anymore a role in the further deposition of particles. Under these conditions only the suspension properties and operational conditions will determine the relation between back-transport and convective transport.

Two types of cake formation were identified during the present research:

1. A short-term, mainly **reversible cake formation**, which is observed when the critical flux is surpassed. This cake formation produces a usually fast increase in filtration resistance and therefore in the trans-membrane pressure (TMP). If the hydraulic flux is stopped or a back-flux is applied, most of the cake detaches and permeability is mostly restored.
2. A long term **consolidated cake formation** which is formed even when operating the MBR in the range of the observed critical flux, according to its weak definition (Wu *et al.*, 1999). Even if no increase in TMP is observed at the short term (minutes), cake formation seems to slowly occur. As explained in Chapter 4, in systems with a wide distribution of particle size, an average or apparent critical flux is determined. Even though no appreciable increase in TMP is observed within operational cycles, the critical flux for the smaller fraction of particles may be surpassed, allowing slow deposition. With time, cake develops and consolidates. Owing to its nature, this consolidated cake can be easily removed by a plain physical cleaning operation.

The short term cake formation is the main responsible phenomenon determining the critical flux. The long term cake formation slowly increases the membrane resistance, until a point when the TMP may be too high and a physical cleaning procedure is required.

Cake formation is determined to a high extent by the properties of the sludge (see Figure 7.16). A decrease in particle size showed a remarkable enhancing effect on the degree of particle deposition. This proved to be of high importance for the feasibility of thermophilic anaerobic submerged MBRs, since reduction in particle size, most likely due to cell decay, showed to have a detrimental effect over the flux (Chapter 5). When particle size is reduced, not only the magnitude of the flux is affected, but also the rate of resistance increased when the critical flux is surpassed. This is due to a higher specific cake resistance. This effect is clear when comparing the performances of the mesophilic and thermophilic submerged MBRs, presented in Chapters 4 and 5.

Cake formation can be controlled by increasing the surface shear. Surface shear is an efficient way of controlling particle deposition, as long as it does not affect suspension properties. However, usually this is not the case, since high shear rates will most likely reduce particle size, increasing particle deposition, a situation that is regarded in Chapter 7 as “the shear rate dilemma”.

9.4. THE SHEAR RATE DILEMMA

Since cake formation proved to be by far the main factor limiting the flux, an increase in the surface shear is the logic alternative to reduce particle deposition, and enhance membrane filtration. However, as schematically represented in Figure 9.1, increases in shear rate, and therefore in shear stress, will most likely disrupt the biological flocs, reducing particle size. As already discussed, this will increase particle deposition due to a decrease in back-transport, limiting the applied flux. Results presented in Chapter 7 confirm this phenomenon. The challenge lies on looking for conditions under which surface shear is enhanced, without exposing the sludge to levels of shear stress that can reduce the size of the flocs or induce cell disruption. The search for these conditions should include the evaluation of different reactor configurations or membrane disposition. The applied shear rate then represents a variable that requires optimization. It has to be provided at a level that sufficiently prevents particle deposition, without strongly affecting the suspension properties.

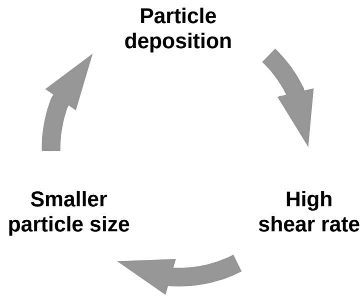


Figure 9.1: The shear rate dilemma.

9.5. THERMOPHILIC ANAEROBIC MBRS

An important part of the experiments performed in the framework of this thesis was focused on studying the feasibility of MBR technology to thermophilic anaerobic conditions. In general, high temperature operation positively affects membrane filtration, due to the temperature effect on the rheology of both permeate and sludge. A lower sludge viscosity means that lower shear rates will suffice for providing the same shear stress, resulting in lower energy requirements. A lower permeate viscosity increases membrane permeability, decreasing the trans-membrane pressure. These effects were evidenced by experiments presented in Chapter 2, showing a better filtration performance for the thermophilic MBR compared to the mesophilic MBR. However, changes in the retained solids properties showed a deep impact on the filtration performance of the thermophilic reactor. Changes in particle size, most likely induced by high cell decay rates resulting in an accumulation of cell fragments, showed to be of great importance in determining the critical flux and also the supra-critical TMP increase rate. This is clear when comparing scanning electron microscope (SEM) images of the cake layer formed over the membranes surface, during the operation of the submerged MBRs operated under thermophilic (Chapter 5) and mesophilic (Chapter 4) conditions. Figure 9.2 shows that the cake layer formed under thermophilic conditions was composed of extremely small particles, in comparison with the cake observed under mesophilic conditions. Indeed, almost no cells can be observed forming the cake layer formed in the thermophilic MBR. Due to a lower degree of back-transport, smaller particles preferentially deposit over the membrane surface, decreasing the critical flux and forming a cake characterised by a high specific resistance.

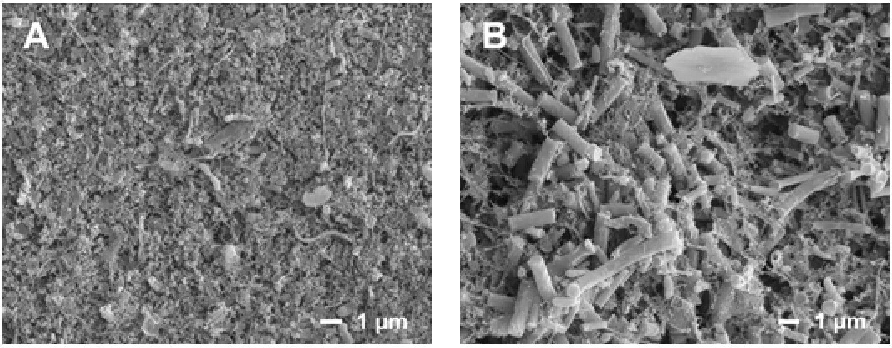


Figure 9.2: SEM images from the cake covering the membrane surface of thermophilic (A) and mesophilic (B) submerged MBRs. Images were taken from Figures 5.7 and 4.6.

As expected, an increase in shear rates resulted in higher critical fluxes. This interrelation is clearly demonstrated by comparing the critical fluxes obtained with the submerged MBR configuration (Chapter 5) with those obtained using the side-stream MBR configuration (Chapter 7). However this flux improvement is achieved at the expense of increased energy requirements. Furthermore, exposure of the sludge to a high shear stress resulted in a high number of smaller particles, as evidenced by the particle size distribution. The latter subsequently affected the applicable fluxes, as discussed above, culminating in the shear rate dilemma. However, long term operation was possible for both configurations, submerged and side-stream, in the absence of chemical cleaning procedures.

9.6. High suspended solids waste streams

The application of anaerobic MBRs to the treatment of wastewaters containing high amount of particulate organic matter was studied in Chapter 6. Thermophilic conditions showed to be positive in increasing the degradation rates, enabling a higher organic loading, while membrane filtration proved to be an effective way of retaining the suspended organic matter. However, it is clear that membrane filtration only represents a physical separation device. Organic matter degradation rates are dependent on the concentration of active microorganisms and a reactor overload obviously results in an accumulation of unconverted solids inside the reactor. Such accumulation subsequently dilutes the active biomass, and reduces the stability of the entire treatment system. In fact, total solids retention in MBR systems reduces the applicable organic loading rates, when compared to those applied in treatment systems that allow wash-out of solids. For instance, in granular sludge bed or biofilm systems, part of the suspended solids may not be retained or degraded, leaving the reactor without treatment. Therefore, performances comparison between MBR systems and granular sludge bed and/or biofilm systems has to be done based on their conversion capacities instead of the applied loading rates.

Only low flux values were achieved during the operation of both thermophilic and mesophilic MBRs. By the end of the operation, critical fluxes under both temperature conditions were below 7 $L/m^2{\cdot}h$. Increases in gas flow rate were not effective in enhancing the critical flux. Further research is needed in order to determine conditions that enable higher operational fluxes.

9.7. APPLICATION OF MBR TECHNOLOGY TO SALINE WASTEWATER TREATMENT

MBR technology represents a highly efficient option for biomass retention, offering a reliable way to retain specific microorganisms, even if they do not have the capacity of forming aggregates. High salinity has shown to be a harsh condition for biomass immobilization by biofilm formation. The results presented in Chapter 8 indicate that membrane filtration is an effective way to retain active bacteria that would wash-out in the traditional granular sludge bed reactors. Enhanced membrane biomass retention offers also the possibility to retain very specific microorganisms, opening interesting opportunities for the use of specific inocula, such as microorganisms obtained form natural saline environments (Vallero *et al.*, 2005). During the present research no problems of scaling over the membrane surface were detected. However, depending on the media composition and operational pH, this eventually may represent a point of concern.

9.8. EFFECT OF SUBSTRATE ACIDIFICATION LEVEL

The level of substrate acidification greatly affected the physical sludge properties, as shown in Chapters 5 and 7. When feeding non-acidified substrates, the sludge was characterised by a high apparent viscosity, as a result of the development and complete retention of acidogenic bacteria. Acidogenic bacteria grew mainly as single cells, not associated to flocs, and thus strongly contributing to a reduction in particle size. Low particle size and high apparent viscosity were most likely the main reasons for the observed low attainable fluxes when feeding the reactors with non-acidified substrates. This was observed under both reactor configurations tested, i.e. submerged and side-stream MBRs. Results presented in Chapters 5 and 7 clearly demonstrate that wastewater composition drastically impacts the biomass microbial variety, which subsequently determines the physical properties of the sludge, strongly affecting the attainable fluxes. Therefore, it is not possible to extrapolate membrane performance data obtained with a particular substrate to a different application.

9.9. REACTOR CONFIGURATION

Side-stream or submerged? This is probably one of the most frequently asked questions when dealing with MBR technology. Several factors influence the final decision. For aerobic

MBRs, submerged configurations are favoured, owing to the relative low energy requirement compared to the side-stream configuration. For anaerobic MBRs, however, the situation is not yet clear. Due to the low bacterial growth rates, anaerobic MBRs need to be operated at higher biomass concentrations in order to provide an efficient treatment at high organic loading rates. Under these conditions, cake layer formation has shown to be the key factor determining the permeate flux. Minimizing cake layer formation by applying higher shear rates resulted in higher permeate flux in side-stream MBRs. However, changes in sludge properties likely off-sets the benefits of the high surface shear, creating the operational shear rate dilemma.

Figure 9.3 presents the sum of the costs derived from membrane acquisition/replacement and energy requirements, as a function of the applied flux, for submerged and side-stream configurations. Assumptions for calculations were the same as those made for the evaluations presented in Figures 5.15 and 7.14, considering the use of tubular membranes. Membrane lifetime and price were considered to be 5 years and 125 €/m^{2*}, respectively. It is clear that for both configurations the calculated costs strongly depends on the applied flux. The side-stream configuration involves higher operational costs due to higher energy requirements. During our research, higher fluxes were achieved using the side-stream configuration. However, it has to be noticed that the side-stream MBR operation proceeded at a lower biomass concentration than the submerged MBR. Costs evaluation, considering the fluxes achieved during the present research, gives values about 0.46 and 0.30 €/m^3 of permeate for the submerged and the side-stream configuration, respectively.

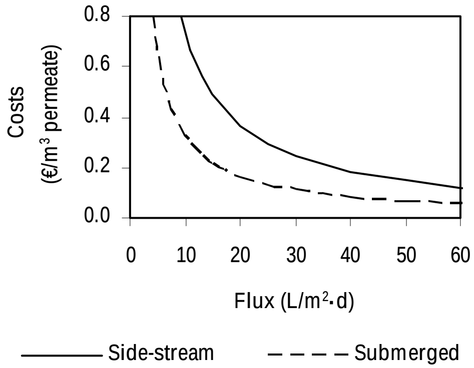


Figure 9.3: Costs derived from membrane acquisition/replacement and energy requirements for gas sparging (submerged MBR) and liquid cross flow (side stream MBR). Membrane lifetime and price were considered to be 5 years and 125 €/m^2 respectively. Assumptions for calculations were the same as those for Figures 5.15 and 7.14.

The development of aerobic MBR technology has certainly enabled the development of an important market for membrane production. Membrane prices has

* Norit, personal communication (2007)

dropped considerably during the last decade. For example, Kubota flat sheet membranes costs are currently in the range of 50 €/m^2 (Judd, 2006). If the latter values is used to re-calculate the costs of the submerged configuration, the membrane/energy costs will reduce from 0.46 to 0.21 €/m^3 of permeate. When considering the fluxes obtained during the operation of the mesophilic submerged MBR, i.e. 20 L/m^2·h, a value of only 0.08 €/m^2 is obtained. Costs evaluations are also influenced by membrane lifetime. Recent studies have suggested longer membrane lifetimes than what was originally expected, i.e. over 10 years (De Wilde *et al.*, 2007), which is twice the value assumed for the costs considerations presented in Figure 9.3. Anaerobic MBR technology is still on its developing stage, requiring more research in order to determine the optimum conditions and configurations that enable its efficient and economically feasible application

Most of the conducted research dealing with anaerobic MBRs has been performed using completely mixed bioreactors, equipped with a membrane separation device either in a submerged or in a side-stream c0nfiguration. However, some authors have suggested the use of other reactor types, such as biofilm reactors or granular sludge bed reactors, in combination with micro or ultra filtration membranes (Bailey *et al.*, 1994; Liao *et al.*, 2006; Lew *et al.*, 2007). The reasoning underlying this approach is to produce solids free effluents when operating granular sludge bed reactors, and/or promote the retention of an undetermined part of the biomass in the form of biofilms or granules so the membrane is exposed to only a fraction of the sludge. However, such approach intrinsically eliminates the bacterial selection pressure, which has proven to be a determining factor in the formation of biofilms and granules. Apparently, the fundamental concepts of granulation and biofilm formation were not taken into account when proposing this concept. Very likely, granules and/or biofilms will at least partially disintegrate under the non-selective conditions after prolonged periods of time. Disintegration of the morphological sludge structure will even manifest more rapidly when extreme conditions prevail, i.e. conditions of particular interest for MBR application. Moreover, our results indicate that the properties of a specific fraction of the sludge can determine the overall filtration performance behaviour of the entire system (Chapters 5 and 7). Indeed, the presence of a fraction of small particles can negatively affect the attainable flux, even if its concentration is moderate or low. During the research described in Chapter 8, a UASB reactor operated at high saline conditions was coupled with a microfiltration membrane module, to achieve complete biomass retention. Even though solids concentration in contact with the membrane were very low, lower than 2 g/L, operational fluxes were only in the range 10-12 L/m^2·h. This confirms that not only the quantity but also the quality of the solids are of vital importance in defining filtration performance in MBR systems.

9.10. RECOMMENDATIONS FOR FURTHER RESEARCH

Anaerobic MBR represents a developing technology. It certainly offers several technical advantages in comparison with traditional anaerobic reactors, particularly in those situations where sludge granulation and/or immobilization cannot be guaranteed. However, research is still required in order to determine the conditions that also enable its economical feasibility. Flux enhancement is definitively a key factor that should receive special attention, since membranes themselves are still a determining factor in the cost balance.

During the present research only tubular membranes were tested. Flat sheet and hollow fibers membranes performances need to be tested. Gas slug flow regime has proved useful in enhancing filtration in aerobic MBRs. Even though it failed to provide high fluxes in the short term tests presented in Chapter 5, further research is needed in order to asses its potential application.

The double effect of shear rate observed during this thesis, being regarded as the shear rate dilemma, requires further study. Shear rate most likely is a variable that can be optimized, as already discussed. Therefore, research on the effects of shear stress on the integrity of anaerobic flocs, and on microbial viability is of great interest. This information can lead to the correct selection of circulating pumps and fitting for side-stream MBRs. The influence of reactor hydrodynamics on surface shear stress needs further research. Simulation tools, like computational fluid dynamics (CFD), and experimental determination using developed shear probes (Bérubé *et al.*, 2006) could be applied for that purpose.

Cake formation, the limiting factor for the application of anaerobic MBRs, is strongly determined by the sludge properties. Therefore, the modification of suspension properties may be a solution for increasing applicable fluxes. The use of flocculants has proven effective in aerobic MBRs in this sense. Flocculants dosage frequency in aerobic MBRs is related with their biodegradability and the sludge age, since flocculants are removed from the reactor with sludge wastes. Anaerobic systems operate at high sludge ages, so this parameter most likely will not play a role in determining dosage frequency. The use of flocculants as a way to control particle size, and therefore cake formation, in anaerobic MBRs has not yet been reported.

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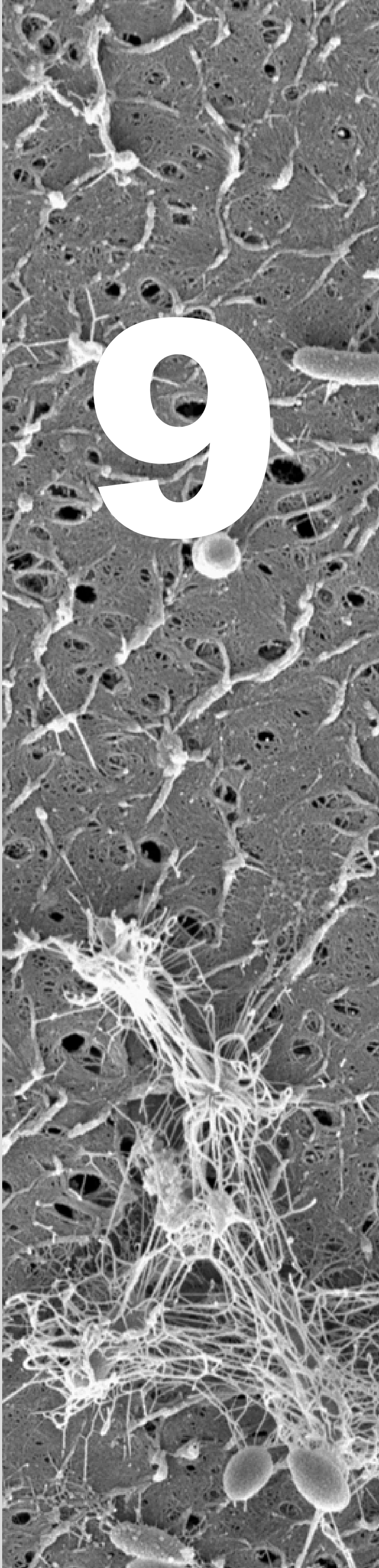
9

Samenvatting en algemene discussie



9.1. TOEPASSING VAN ANAEROBE MBRS

Biomassaretentie is essentieel voor een succesvolle en kosteneffectieve toepassing van de hoogbelastbare anaerobe technologie voor afvalwaterbehandeling. De meest voor de handliggende strategie voor een efficiënte biomassaretentie is de vorming van slibvlokken, biofilms en korrelsib. Hoewel alle details nog niet eenduidig worden begrepen geven de huidige inzichten voldoende handvaten om korrelslibgroei en biofilmvorming op een relatief eenvoudige manier te bewerkstelligen. Hierdoor is het mogelijk om anaerobe reactoren te bedrijven met zeer hoge actieve biomassaconcentraties, resulterend in een hoge omzettingscapaciteit, zelfs bij zeer hoge hydraulische belastingen.

Anaerobe zuivering wordt momenteel toegepast op zeer diverse afvalwaters, die meestal afkomstig zijn van de voedingsmiddelenindustrie. Een recente telling geeft ongeveer 2300, door bedrijven geregistreerde, anaerobe installaties (van Lier, 2007). Afvalwater uit de voedingsmiddelenindustrie wordt gekarakteriseerd door een redelijk hoge concentratie organisch materiaal met een relatief hoge biologische afbreekbaarheid. Naast deze afvalwaters zijn er echter diverse stromen waarbij anaerobe zuivering minder succesvol is, meestal te wijten aan slechte biomassaretentie. Extreme condities, zoals hoge zoutgehaltes, extreme temperaturen, het vóórkomen van specifieke toxische verbindingen, oppervlakte actieve stoffen en/of chelerende verbindingen, leiden vaak tot de vorming van gedispergeerd slib, dat aan uitspoeling onderhevig is. Door de enorme waterbesparingen en de strategie naar kringloopsluiting in de industrie, zal naar verwachting het aantal extreme afvalwaters in de nabije toekomst toenemen. Indien, voor deze afvalwaters, slibuitspoeling limiterend wordt, biedt de op membraanscheiding gebaseerde biomassaretentie een alternatief om de actieve biomassa in de anaerobe reactor te houden.

Alhoewel de toepassing van membranen gepaard gaat met een hoge efficiëntie, is het onvermijdelijk dat hier ook hoge operationele- en investeringskosten mee gepaard gaan in vergelijking met korrelslib- of biofilmtechnologie. De haalbaarheid van een anaerobe membraan bioreactor (MBR) is daarom direct te relateren aan de potentiële technisch-economische voordelen van op membraanscheiding gebaseerde biomassaretentie. Naar verwachting zullen anaerobe MBR systemen met name interessant zijn bij bovengenoemde extreme afvalwaters wanneer slibimmobilisatie moeilijk of niet verloopt.

Behandeling van afvalwater met hoge concentraties aan vaste en zwevende stof is eveneens van belang gezien het feit dat deze stoffen volledig door het membraan worden teruggehouden. Andere uitdagingen liggen in het accumuleren van specifieke bacteriën die in staat zijn om recalcitrante en/of moeilijk afbreekbare stoffen om te zetten. De combinatie van een anaerobe MBR met andere postmembraan systemen, biedt mogelijkheden om een aerobe nazuiveringstap volledig weg te laten. De huidige trend in de industrie om het specifieke waterverbruik te verlagen waardoor afvalwaters geconcentreerder worden zullen ongetwijfeld het marktpotentieel van anaerobe MBRs vergroten.

De beste perspectieven voor toepassing van anaerobe MBRs liggen bij hoog geconcentreerde afvalwaters, gezien het feit dat de flux van een MBR hydraulisch gelimiteerd is. De concentratie aan organische vuillast en de volumetrische omzettingcapaciteit van de reactor bepalen in grote mate de hydraulische retentietijd, die in feite de permeaatstroom bepaalt. Voor elke gegeven flux, bepaalt de permeaatstroom de benodigde dimensies van de membraaninstallatie en zal dus een directe invloed hebben op de operationele- en investeringskosten. De economische haalbaarheid zal altijd sterk afhankelijk blijven van de geldende membraanprijzen en de toepasbare fluxen, ook al zal anaerobe MBR technologie voor laag geconcentreerde afvalwaters technisch haalbaar worden.

9.2. MICROBIOLOGISCHE ACTIVITEIT EN SYNTROFE INTERACTIES

Een van de potentiële nadelen van MBRs is dat ze meestal gebaseerd zijn op ideaal gemengde reactoren met gedispergeerde biomassa dat betekent dat het slib aanwezig is in de vorm van zeer kleine vlokken of zelfs losse cellen. Biofilms en korrelslib bestaan uit hechte conglomeraties van verschillende micro-organismen, waarbij de afstanden tussen de bacteriën minimaal zijn. Door deze kleine onderlinge afstanden vindt er een zeer efficiënt transport plaats van tussenproducten, waarbij potentieel remmende stoffen, zoals waterstof, efficiënt worden weggevangen door methanogenen. Deze zogenaamde syntrofe interacties zijn essentieel voor een goed lopend gistingsproces. Verschillende auteurs wijzen op het verstoren van deze syntrofe interacties door de hoge mengingsgraad in MBR systemen, als gevolg waarvan het gistingsproces maar ten dele verloopt (McMahon *et al.*, 2001; Kim *et al.*, 2002). Brockmann en Seyfried (1997) stelden zelfs dat de waargenomen lagere specifieke slibactiviteit in een anaerobe MBR, het resultaat zou zijn van de hoge afschuifkrachten op de membraanfilters. Toch is er tijdens het huidige onderzoek geen significant bewijs gevonden dat bedrijfsvoering met dispers slib de specifieke biologische activiteit nadelig beïnvloedt. Mogelijk wordt het negatieve effect van het dispergeren van het methanogene slib gecompenseerd door het ophopen van hoge concentraties actieve biomassa. Daarbij vindt door de aanwezigheid van zeer kleine deeltjes en losse cellen een zeer efficiënt massatransport plaats vanuit de bulk van de vloeistof naar de bacteriën. De aangelegde specifieke slibbelasting van een mesofiele ondergedompelde MBR (hoofdstuk 4) was verrassend hoog, bij een deeltjesgrootte kleiner dan 100 µm voor 85% van het slib. Kennelijk, was deze vlokgrootte voldoende om de juiste condities voor een efficiënt transport van tussenproducten tussen de verschillende bacteriën mogelijk te maken. Ook het bedrijven van een zijstroom MBR met hoge doorstroomsnelheid (tot 1.5 m/s) gaf geen enkele aanleiding om het gesuggereerde negatieve effect van hoge afschuifkrachten op de specifieke slibactiviteit te ondersteunen (Hoofdstuk 7). De waargenomen specifieke methanogene activiteit (SMA) was vergelijkbaar met gerapporteerde waarden van biomassa in de vorm van biofilms of korrelslib. Dit houdt in dat anaerobe conversie van organisch materiaal effectief kan plaatsvinden in een MBR, zonder de aanwezigheid van biofilms of korrelslib. Mogelijk zal bij een té hoge afschuifspanning de slibactiviteit wel afnemen. Binnen het onderhavige onderzoek is daarom gewerkt met een zijstroom MBR zonder tegendruk ventielen en doorstroomsnelheden van 1,5 m/s.

9.3. KOEKLAAG VORMING: DE LIMITERENDE FACTOR VOOR DE TOEPASBARE FLUX

Het onderhavige onderzoek richtte zich op de haalbaarheid van anaerobe MBR systemen bij verschillende configuraties, substraten en temperaturen. Opvallend was dat onder alle omstandigheden de koeklaagvorming de kritieke parameter bleek te zijn voor de toepasbare flux. Mogelijk is dit te wijten aan de toegepaste hoge biomassa concentraties van meer dan 20 g droge stof (TSS)/l. Onder alle onderzochte condities werd slechts een zeer lage mate van onomkeerbare vervuiling gevonden. Dit betekent dat lange termijn bedrijfsvoering van een anaerobe MBR mogelijk is zonder daarbij chemische reinigingen uit te voeren. Deze resultaten zijn van cruciaal belang omdat chemische reinigingsprocedures de bedrijfsvoering beïnvloedt en het ex-situ onderhoud aan membranen noodzakelijk maakt. Een lage frequentie van chemische reiniging zal hoogstwaarschijnlijk ook in een langere membraanlevensduur resulteren. Dit laatste is uiteraard bepalend voor de financiële haalbaarheid, aangezien membraanvervanging een van de belangrijkste kostenposten is voor de toepassing van MBRs.

De minimale porievervuiling is waarschijnlijk te danken aan deze koeklaagvorming. Indien het membraan bedekt is door een koeklaag wordt het niet langer blootgesteld aan de reactorinhoud, waardoor porievervuiling en andere vervuilingmechanismen niet of nauwelijks voorkomen. De koeklaag zorgt er ook voor dat de exacte samenstelling van het membraan en de exacte poriegrootte een veel minder significante rol spelen in het bepalen van de toepasbare flux dan van te voren werd aangenomen. Zodra het membraanoppervlak bedekt is met een koeklaag van slib, spelen de eigenschappen van het membraan ook geen verdere rol meer in de depositie van deeltjes op het membraan of op de koeklaag. Onder deze omstandigheden zijn het de eigenschappen van de oplossing, slib en de operationele condities die de relatie bepalen tussen het membraan afwaarts gerichte transport van deeltjes (back-transport) en de convectieve aanvoer van deeltjes.

In dit onderzoek zijn twee typen koeklaagvorming geïdentificeerd:

1. De instantane vorming van een koeklaag die wordt waargenomen als de kritische flux overschreden wordt en die vrijwel geheel verwijderbaar is tijdens terugspoelen. Deze zgn. 'korte termijn' koeklaag resulteert in een snelle toename van de filtratieweerstand en dus in een toename van de transmembraandruk (TMD). Als de hydraulische flux wordt gestopt of als er een terugspoeling wordt toegepast, wordt het grootste gedeelte van de koeklaag losgeslagen en de permeabiliteit van het membraan hersteld.
2. De langzame vorming van een op de lange termijn consoliderende koeklaag vindt plaats wanneer de MBR bedreven wordt in de buurt van de kritieke flux (Wu *et al.*, 1999). Zelfs als er geen korte termijn toename van TMD wordt waargenomen, vormt zich langzaam toch een steeds dichtere koeklaag. Afhankelijk van de deeltjesgrootteverdeling leidt bedrijfsvoering in de buurt van de kritische flux tot verdichting van de koeklaag. De deeltesgrootteverdeling van een operationele MBR systeem heeft normaliter een brede bandbreedte (hoofdstuk 4). Hierdoor kan de kritieke flux voor een specifiek gedeelte van de kleinere deeltjes toch worden overschreden, waardoor koeklaagverdichting langzaam optreedt. Na verloop van tijd ontwikkelt zich een geconsolideerde koeklaag die moeilijker met terugspoeling is te verwijderen. Echter, door zijn fysische

eigenschappen kan ook deze koeklaag met eenvoudig fysische reiniging worden verwijderd.

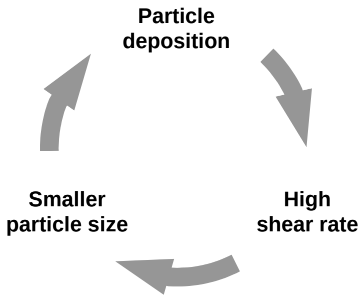
De ‘korte termijn’ koeklaag is echter de belangrijkste factor die de kritieke flux bepaald. De koeklaag gevormd op de langere termijn verhoogt langzaam de membraanweerstand tot dat de TMD te groot wordt en er een fysische reiniging noodzakelijk is om de permeabiliteit te herstellen.

De vorming van de koeklaag wordt in grote mate bepaald door de eigenschappen van het slib (zie Figuur 7.16). Een afname in deeltjesgrootte leidt tot een grotere depositie op en in de koeklaag en leidt vervolgens tot een snelle verdichting van de gevormde koeklaag. De deeltjesgrootteverdeling is daarom van doorslaggevende betekenis voor de haalbaarheid van anaerobe MBRs. Onder thermofiele condities werd een enorme reductie in de deeltjesgrootteverdeling gevonden, waarschijnlijk door afsterving van cellen, hetgeen leidde tot een zeer compacte koeklaag, resulterend in een zeer lage kritische flux (Hoofdstuk 5). Bij een afnemende deeltjesgrootte wordt niet alleen de ordegrootte van de flux beïnvloedt, maar ook de verandering van de weerstand als gevolg van kritieke flux overschrijding, wat een gevolg is van de ontstane hogere specifieke koeklaagweerstand. Deze verandering in koeklaagweerstand verklaart in feite de grote verschillen in verkregen bedrijfsvoering van de mesofiele en thermofiele ondergedompelde MBRs, zoals gepresenteerd in hoofdstuk 4 en 5.

Koeklaagvorming kan worden gecontroleerd door verhoging van de oppervlakte afschuifspanning, de zgn. “shear”. De toe te passen afschuifkracht is een efficiënt middel om de deeltjesdepositie in de koeklaag te beheersen, zo lang de eigenschappen van de oplossing niet worden beïnvloed. Echter, meestal is dit wel het geval, omdat hoge afschuifkrachten logischerwijs ook de deeltjes verkleinen en daarmee deeltjesdepositie weer doen toenemen . Deze tegenstrijdige situatie wordt omschreven in hoofdstuk 7 als “the shear rate dilemma”.

9.4. “THE SHEAR RATE DILEMMA”

Omdat koeklaagvorming veruit het grootste effect heeft op de flux, is het logisch om te veronderstellen dat een toename in de oppervlakte afschuifspanning de deeltjesdepositie kan reduceren. Echter, zoals schematisch weergegeven in Figuur 9.1, leidt een verhoging van de afschuifkracht, en dus een toename in de afschuifspanning, ook tot verstoring van de biologische vlokvorming, waardoor de deeltjesgrootte weer afneemt. Zoals eerder besproken leidt dit tot een verhoogde deeltjesdepositie, doordat het membraan afwaarts gerichte transport van kleine deeltjes afneemt, waardoor de flux niet verder zal/kan toenemen. Resultaten die dit fenomeen bevestigen zijn gepresenteerd in hoofdstuk 7. Het is de uitdaging om condities te vinden die de oppervlakte afschuifspanning maximaliseren, maar het slib niet blootstellen aan een dusdanige afschuifspanning die de deeltjesgrootte verder doet afnemen. Optimalisatie van de toe te passen afschuifkracht is afhankelijk van de exacte reactor configuratie en de verkregen slibeigenschappen. Nader onderzoek voor een specifieke situatie zal zich moeten richten op het vinden van een relatie tussen de toegepaste afschuifkracht en de verkregen koeklaag. Ofwel, er dient een doorstroomsnelheid en afschuifspannning te worden gevonden die koeklaagverdichting voorkomt en anderzijds de eigenschappen van de biomassa niet teveel aantast.



Figuur 9.1: The shear rate dilemma.

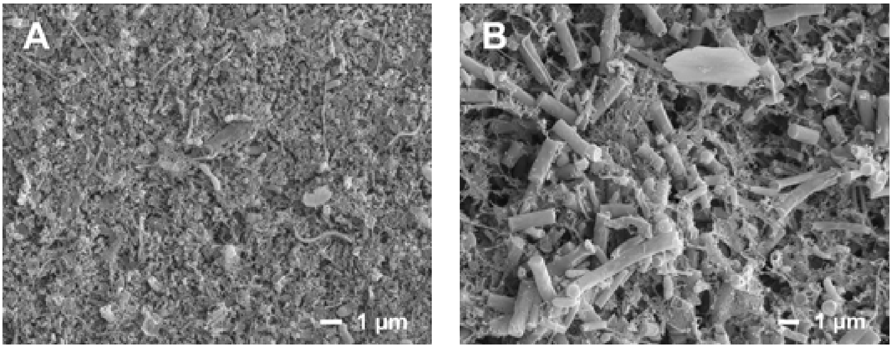
9.5. THERMOFIELE ANAEROBE MBR'S

Een groot gedeelte van de uitgevoerde experimenten richtte zich op de haalbaarheid van de MBR technologie onder thermofiele condities. Normaliter zullen hogere temperaturen de bedrijfsvoering van membraanfiltratie positief beïnvloeden vanwege het temperatuureffect op de rheologie van zowel het permeaat als het slib. Door de resulterende lagere viscositeit zijn er lagere afschuifkrachten nodig om voldoende afschuifspanning op te wekken en dus zal ook het energieverbruik lager zijn. Ook leidt een lagere viscositeit tot een hogere membraan permeabiliteit waardoor de TMD zal afnemen. Deze effecten zijn experimenteel vastgesteld en beschreven in hoofdstuk 2, waarbij een thermofiele MBR een veel betere membraanfiltratie liet zien dan de mesofiele reactor. Toch blijken de veranderingen in de slibeigenschappen juist de filtratieprestatie van de thermofiele reactor op de lange termijn te bepalen. Veranderingen in de deeltjesgrootte, waarschijnlijk als gevolg van de hogere afsterving van cellen en ophoping van cel fragmenten, blijkt van doorslaggevend belang te zijn bij het bepalen van de kritieke flux en de super-kritische vervuilingsnelheden. Het grote verschil in deeltjesgrootteverdeling heeft direct zijn weerslag op de koeklaagsamenstelling (hoofdstuk 4 en 5). Scanning elektronische opnames (SEM) laten een enorme verdichting zien onder thermofiele condities (Figuur 9.2).

Zeer opvallend is de afwezigheid van volledige cellen in de koeklaag gevormd onder thermofiele condities. Mogelijk zijn de waargenomen celfragmenten eveneens afkomstig uit het origineel mesofiele entmateriaal. Door de lagere membraan afwaarts gerichte transport van deeltjes, zullen de kleinere deeltjes zich steeds meer ophopen in de koeklaag, zodat er een koeklaag met een hoge specifieke weerstand wordt gevormd en de kritieke flux daalt.

Bij een min of meer gelijke deeltjesgrootteverdeling leiden grotere afschuifkrachten tot hogere kritische fluxen. Deze relatie is experimenteel bevestigd en kan worden afgeleid door de waarden van de behaalde kritische fluxen te vergelijken van de ondergedompelde MBR configuratie (hoofdstuk 5) en de zijstroom MBR configuratie (hoofdstuk 7). In de laatst genoemde reactor is de verkregen flux hoger ten koste van een toenemend energieverbruik. Echter, blootstelling van het slib aan hogere afschuifspanningen leidt tot meer kleinere deeltjes, wat ook door de deeltjesgrootteverdeling wordt aangegeven. Deze verdeling beïnvloedt weer de toepasbare flux zoals omschreven in "the shear rate dilemma".

Uit de verkregen resultaten kan verder worden geconcludeerd dat bedrijfsvoering op de lange termijn mogelijk is zonder chemische reinigingsprocedures. Dit geldt voor zowel de ondergedompelde als de zijstroom configuratie.



Figuur 9.2: SEM foto's van een koeklaag die het membraanoppervlak bedekt onder thermofiele (A) en mesofiele (B) omstandigheden in anaerobe MBRs. De foto's komen van Figuur 5.7 en 4.6.

9.6. AFVALWATERS MET HOGE ZWEVENDE STOF GEHALTES

Behandeling van afvalwater met een hoge concentratie van zwevende stof in een anaerobe MBR is beschreven in hoofdstuk 6. Het toepassen van thermofiele condities verhoogt de biologische afbraaksnelheid, waardoor een hogere organische slibbelasting en volume belasting kan worden toegepast. Bovendien is membraanfiltratie een effectieve manier om alle zwevende stof tegen te houden. Het is duidelijk dat membranen enkel een fysisch scheidingsmechanisme zijn en dat de daadwerkelijke afbraak van het organische materiaal afhankelijk is van de concentratie actieve biomassa. Een overbelasting van de reactor leidt direct tot accumulatie van niet omgezet organisch materiaal. Een dergelijke ophoping verdunt de actieve biomassa en reduceert de stabiliteit van het gehele systeem. In vergelijking met systemen waarbij een selectieve uitspoeling van zwevende stof mogelijk is, leidt het effectief terughouden van zwevende stof in MBR systemen feitelijk tot een reductie van de toepasbare volumebelastingen. In korrelslib reactoren of biofilm systemen zal een deel van de zwevende stof de reactor echter verlaten zonder omgezet te zijn. Reactorprestaties dienen daarom vergeleken te worden op basis van de behaalde CZV conversies en niet op basis van toegepaste volumebelastingen.

Duurproeven met zowel thermofiele en mesofiele MBRs leverden tegenvallende lage fluxen bij voeding met hoge zwevende stofgehaltes. De geobserveerde kritische fluxen waren niet hoger dan 7 $L/m^2{\cdot}u$. Het verhogen van de gassnelheid had geen significant verhogend effect op de kritische flux. Nader onderzoek is noodzakelijk om te kunnen bepalen onder welke condities hogere operationele fluxen bij hoge zwevende stof gehaltes mogelijk zijn.

9.7. De toepassing van de MBR technolgie op zout afvalwater

Afvalwater met hoge zoutgehaltes zijn limiterend voor de vorming van biofilms en of slibkorrels. De resultaten gepresenteerd in hoofdstuk 8 laten zien dat membraan gebaseerde biomassa retentie een effectieve manier is om specifieke actieve bacteriën in het systeem te houden, die in anaerobe slibbed reactoren zouden uitspoelen. De membraan gebaseerde biomassa retentie biedt hierdoor ook de mogelijkheid om heel specifieke inocula te gebruiken, zoals afkomstig uit natuurlijke zoute leefmilieus (Vallero *et al.*, 2005). Gedurende dit onderzoek zijn er geen problemen ondervonden met anorganische neerslag van de zouten op het membraanoppervlak. Echter dit is wel een punt van aandacht, aangezien kleine afwijkingen in de pH of de samenstelling van het medium kunnen leiden tot het overschrijden van oplosbaarheidproducten en dus tot storende neerslagen.

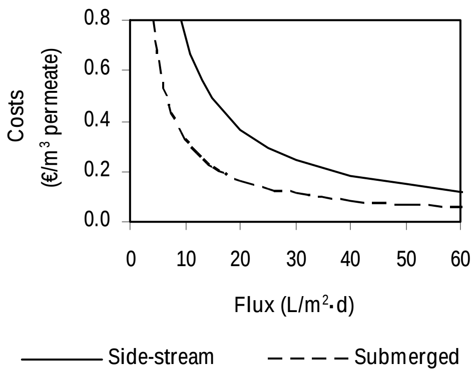
9.8. Effect van de mate van voorverzuring van het substraat

De mate van voorverzuring van het substraat heeft een grote invloed op de fysische slibeigenschappen, zoals beschreven in hoofdstuk 5 en 7. Aanwenden van gedeeltelijk verzuurd substraat leidde tot groei van slib met een zeer hoge viscositeit, waarschijnlijk door het volledig terughouden van de acidogene bacteriepopulatie inclusief de uitgescheidde producten. Acidogene bacteriën groeien dispers als losse cellen, niet gebonden aan vlokken, en dus leveren ze een sterke bijdrage aan de reductie van de gemiddelde deeltjesgrootte van het slibmengsel. De kleine deeltjesgrootte en de hoge viscositeit vormden samen de belangrijkste reden voor de geobserveerde lage flux bij dit type substraat. Dit was het geval in zowel het ondergedompelde als het zijstroom systeem. De resultaten geven duidelijk aan dat de samenstelling van het afvalwater een enorme impact heeft op de microbiële variëteit, die op zijn beurt de eigenschappen van het slib bepaalt en daarmee de toepasbare fluxen. Daarom zal er bij het extrapoleren van de membraanprestaties altijd rekening gehouden moeten worden met de exacte samenstelling van het gebruikte substraat en kunnen toepassingen op verschillende afvalwaters nooit direct met elkaar vergeleken worden.

9.9. Reactor configuratie

Zijstroom of ondergedompelde membranen? Dit is een van de meest voorkomende vragen wanneer er over de MBR technologie wordt gesproken. Bij toepassing van een aerobe MBR, heeft de ondergedompelde variant de voorkeur, vanwege de relatief lage energieconsumptie in vergelijking tot de zijstroom configuratie. Voor de anaerobe MBR, is dit nog verre van duidelijk. Doordat anaerobe bacteriën een veel lagere groeisnelheid hebben, dient een anaerobe MBR met een hoge biomassa concentratie te worden bedreven om een hoge belastbaarheid mogelijk te maken. Onder deze omstandigheden, zal de koeklaagvorming allesbepalend zijn voor de toepasbare flux. Door hogere afschuifkrachten toe te passen kunnen hogere permeaatfluxen worden gerealiseerd in zijstroom MBR configuraties. Maar een hogere afschuifkracht beïnvloedt de slibeigenschappen op een dusdanige wijze dat de voordelen van hogere afschuifsnelheden mogelijk ook weer worden teniet gedaan, zoals boven beschreven in de “shear rate dilemma”.

Figuur 9.3 beschrijft de kosten voor membraan aanschaf/vervanging en energieverbruik, als functie van de toegepaste flux, voor zowel ondergedompelde als zijstroom configuraties. De aannames gebruikt voor de achterliggende berekeningen zijn dezelfde als voor de evaluaties gepresenteerd in de Figuren 5.15 and 7.14. De membraanlevensduur en prijs zijn gesteld op respectievelijk 5 jaar en 125 €/m^{2}*. Voor beide MBR configuraties zijn de berekende kosten direct afhankelijk van de toe te passen flux. De zijstroom configuratie laat hogere operationele kosten zien door het hogere energieverbruik. Maar met de zijstroom configuratie worden hogere fluxen behaald, zoals ook is bevestigd in het onderhavige onderzoek. Hierbij moet wel worden vermeld dat deze zijstroom configuraties werd bedreven met een lagere biomassa concentratie dan in de ondergedompelde configuratie. De kostenevaluatie, met in achtneming van de behaalde fluxen in dit onderzoek, geeft waarden van 0.46 en 0.30 €/m^3 permeaat, voor respectievelijk de ondergedompelde en zijstroom configuratie.



Figuur 9.3: Kosten afgeleid van de membraanaanschaf/ vervanging en energieverbruik voor ondergedompelde MBRs met biogasrecirculatie voor koeklaag beheersing en zijstroom MBRs. Voor de membraan levensduur en prijs is er een waarde van respectievelijk 5 jaar en 125 €/m^2 aangenomen. De overige aannames zijn dezelfde als gebruikt voor het genereren van de Figuren 5.15 en 7.14.

De ontwikkeling van de aerobe MBR technologie heeft bijgedragen aan de ontwikkeling van een belangrijke markt voor productie van membranen. Membraanprijzen zijn aanzienlijk afgenomen in het laatste decennium. Kubota flat sheet membranen kosten op dit moment nog rond de 50 €/m^2 (Judd, 2006). Als deze laatste genoemde prijs gebruikt zou worden voor de berekeningen van de ondergedompelde configuratie, zouden de kosten reduceren 0.46 tot 0.21 €/m^3 permeaat. Wanneer de fluxen behaald in de ondergedompelde mesofiele MBR worden gebruikt voor deze berekening, d.w.z. 20 L/m^2·u, zakt de prijs drastisch naar 0.08 €/m^3 permeaat. De berekeningen zijn uiteraard afhankelijk van de

* Norit, persoonlijke communicatie (2007)

membraanlevensduur. Onlang is aangetoond dat een meer dan twee keer zo lange membraanlevensduur, d.w.z. meer dan 10 jaar, momenteel praktisch haalbaar is (De Wilde *et al.*, 2007). Dit leidt vervolgens weer tot een halvering van de berekende volumetrische kostprijs. Omdat anaerobe MBR technologie nog volop in ontwikkeling is, zal vervolgonderzoek moeten uitwijzen wat de ideale condities en configuraties zijn om anaerobe MBR systemen economisch haalbaar te maken.

Het meeste onderzoek naar anaerobe MBRs maakt gebruik van ideaal gemengde bioreactoren met daaraan gekoppeld een membraan in ofwel zijstroom ofwel ondergedompelde configuratie. Diverse auteurs doen momenteel onderzoek naar het gebruik van andere type reactoren, zoals een slibbed reactor, met daaraan gekoppeld een micro of ultra filtratie membraan (Bailey *et al.*, 1994; Liao *et al.*, 2006; Lew *et al.*, 2007). De achterliggende gedachte is het produceren van zwevende-stof-vrij effluent uit een slibbed systeem, of de retentie bevorderen van een onbekende fractie van de aanwezige biomassa. Echter, introductie van membraanscheiding gekoppeld aan slibterugvoer in een (korrel)slibbedreactor, elimineert de bacteriologische selectie druk, die essentieel is voor de vorming van biofilms of korrelslib. Op de lange termijn zal, door afwezigheid van selectiedruk, deze bedijfsvoering waarschijnlijk leiden tot een volledige desintegratie van het slibbed. Mogelijk zijn de fundamentele concepten van de vorming van korrelslib en biofilms niet meegenomen bij het voorstellen van dergelijke concepten. Zodra er met extreme condities wordt gewerkt zal de desintegratie van de morfologische structuur nog sneller plaats vinden, terwijl dit juist de condities zijn die het gebruik van een MBR aantrekkelijk maken. De resultaten gepresenteerd in dit onderzoek geven aan dat de eigenschappen van een specifieke fractie van het slib de filtratieprestaties van het gehele systeem kan beïnvloeden (Hoofdstuk 5 en 7). Zelfs een middelgrote tot lage concentratie kleine deeltjes in het slibbed kan het gedrag van het gehele slibbed op de koeklaag bepalen. Dat niet alleen de slibconcentratie zelf maar juist de fractie met de kleinste deeltjesgrootte bepalend is voor de te behalen flux is nader onderzocht in hoofdstuk 8 aan de hand van een UASB met daaraan gekoppeld een microfiltratie membraan, gevoed met zout afvalwater. Ondanks het feit dat de totale stof concentratie die in contact kon komen met het membraan zeer laag was, d.w.z. lager dan 2 g/L, werden er operationele fluxen behaald van slechts 10-12 $L/m^2 \cdot u$. Dit bevestigt de hypothese dat zowel de kwantiteit als de kwaliteit van doorslaggevend belang kan zijn bij de te behalen filtratieprestaties in een MBR .

9.10. Aanbevelingen voor nader onderzoek

Anaerobe MBR is een technologie die zich nog volop ontwikkelt en biedt diverse mogelijkheden en voordelen ten opzichte van conventionele slibbed reactoren. Dit geldt zeker in situaties waar korrelslibvorming en slibimmobilisatie niet gegarandeerd kunnen worden. Toch, is er nog veel onderzoek nodig om de ideale condities te bepalen waarin de technologie economisch haalbaar is. Het verhogen van de toepasbare flux is een punt dat extra aandacht verdient, omdat membranen zelf nog altijd een voorname kostenpost zijn in het gehele kostenoverzicht.

Gedurende dit onderzoek is louter gebruik gemaakt van buisvormige (tubular) membranen. Voor een correcte vergelijking van prestaties en financiële haalbaarheid verdient het aanbeveling om vergelijkend onderzoek te verrichten naar het aanwenden van vlakke plaat (flat sheet) en holle vezel membranen. Ook de wijze van koeklaagbeheersing dient nader te worden onderzocht. Opwaartse gasbellen in een van binnen naar buitengerichte buisvormig membraan geven goede mogelijkheden tot beheersing van de koeklaag. Dit zgn. “slugflow” principe wordt inmiddels succesvol toegepast in aerobe MBR systemen. Hoewel kortdurende experimenten in het onderhavige onderzoek tegenvielen wat betreft de te behalen fluxen, verdient het aanbeveling om het “slugflow” principe nader te onderzoeken voor anaerobe MBR systemen.

Ook het tweeledige effect van een verhoogde afschuifkracht, aangeduid als de “shear rate dilemma”, dient nader onderzocht te worden. Het is de verwachting dat dit een parameter is die geoptimaliseerd kan worden. Daarom is onderzoek naar de effecten van de afschuifspanning op de morfologie en biologische activiteit van anaeroob slib van groot belang. De verkregen informatie kan leiden tot een betere afstemming van pompen en leidingen in zijstroom MBRs. Ook de invloed van de toegepaste hydrodynamica op de oppervlakte afschuifspanning is een hier aan gerelateerd relevant onderwerp. Simulaties met behulp van het zogenaamde, “computational fluid dynamics” (CFD), en experimentele toetsing met behulp van elektrochemische sondes (Bérubé *et al.*, 2006) kunnen hiervoor worden gebruikt.

De vorming van de koeklaag, de limiterende factor voor de toepassing van anaerobe MBRs, is sterk afhankelijk van de slibeigenschappen. Daarom moet nader onderzoek worden verricht naar de mogelijkheden om deze slibeigenschappen te kunnen wijzigen om zo een bijdrage te kunnen leveren aan het verhogen van de toepasbare fluxen. In aerobe MBRs is het toevoegen van flocculanten erg effectief gebleken. Echter bij deze toepassing blijkt de doseringsfrequentie een grote kostenpost te zijn, gelet op de biologische afbreekbaarheid van de flocculanten maar ook de slibleeftijd. Biologische slecht afbreekbare flocculanten worden uit het systeem afgevoerd met het gevormde spuislib. Anaerobe MBR systemen werken over het algemeen met hogere slibleeftijden, en dus zal deze parameter een minder grote rol spelen bij het bepalen van de doseringsfrequentie. Het gebruik van flocculanten om de deeltjesgrootte en dus koeklaagvorming te beheersen in anaerobe MBRs is tot op heden nog niet gerapporteerd.

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NOMENCLATURE

A	membrane area
C	total biomass concentration expressed as total suspended solids
J	permeate flux
J_C	critical flux
K	cake formation correction factor for cross flow micro-filtration
R	resistance
R_C	cake resistance
R_M	membrane resistance
R_{MAp}	apparent membrane resistance
t	time
V	permeate volume
V_G	gas superficial velocity
V_L	liquid superficial velocity
α	specific cake resistance
η	viscosity

ABBREVIATIONS

AnMBR	anaerobic membrane bioreactor
AnSMBR	anaerobic submerged membrane bioreactor
COD	chemical oxygen demand
CSTR	continuously stirred tank reactor
MBR	membrane bioreactor
MLSS	mixed liquor suspended solids
MWCO	molecular weight cut-off
OLR	organic loading rate
Perm	permeability
SAA	specific acidogenic activity
SMA	specific methanogenic activity
SMP	soluble microbial products
CFMBR	side-stream cross-flow membrane bioreactor
SEM	scanning electron microscope
SMBR	submerged membrane bioreactor
TMP	trans-membrane pressure
TSS	total suspended solids
UASB	upflow anaerobic sludge blanket
VFA	volatile fatty acids
VSS	volatile suspended solids

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