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PROSPECTS FOR FLUX ENHANCEMENT IN ANAEROBIC MEMBRANE BIOREACTORS TREATING SALINE WASTEWATER

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Abstract

Successful high-rate treatment of wastewaters in bioreactors is largely dependent on effective sludge retention. Despite the availability of sludge granulation techniques, physical retention by membranes remains a good option, especially when good sludge granulation cannot be guaranteed. The granulation of anaerobic sludge is, for example, impeded by the effects of sodium on sludge properties, such as a weakened granule strength, which might be attributed to disruption of bivalent cation linkages between extracellular polymeric substances (EPSs) that play a key role in granular sludge stability. Under such conditions, the use of membranes ensures full sludge retention, providing a suspended solids-free effluent. However, the feasibility of using membranes in wastewater treatment, especially under anaerobic conditions, requires major improvements in attainable membrane fluxes. This study has therefore investigated methods to increase the membrane flux of anaerobic membrane bioreactors that are operated under saline process conditions.

Two methods for increasing membrane flux have been tested. The first method involved increasing the shear stress at the surface of the tubular membrane employed, in order to enhance the back transport of foulants from the membrane surface to the bulk solution; slug bubbles and inserts were used to increase the shear stress. The second method involved decreasing the concentration of foulants in the bulk solution through the addition of adsorbents and the use of coagulation. Coagulation was induced by the sodium ions naturally present in saline wastewater and through the direct addition of an aluminum-based coagulant.

The applied gas slug appeared to be unable to adequately control fouling, resulting in rapidly increasing trans-membrane pressures (TMP) when operating at a flux in excess of 16 L/m^2.h, as described in Chapter 2. However, the chemical oxygen demand (COD) removal efficiency did not show any significant deterioration, whereas the specific methanogenic activity (SMA) increased from 0.16 to 0.41 g COD per g volatile suspended solid (VSS) per day. The tubular membrane was subsequently equipped with inert inserts in order to produce locally increased shear stress for enhanced fouling control. Results showed that, following the mounting of the inserts in the membrane tube, the membrane flux increased from 16 L/m^2.h to 34 L/m^2.h. However, the pressure drop along the membrane was also greatly increased and it was therefore concluded that the gas slugs were insufficient to increase the membrane flux and the inserts did not offer a practical solution.

In order to understand why the bubbles did not effectively increase the membrane flux, the mass transfer by the bubbles was quantified through computational fluid dynamics modeling. The model and its results are presented in Chapter 3. The modeling indicated that the mass transfer capacity at the membrane surface was higher at the noses of gas bubbles than at their tails, which is in contrast to the results when water was used instead of sludge. The filterability of the sludge at a given mass transfer rate was found to have a strong influence on the TMP, at a steady flux. The model also showed that the shear stress within the internal space of the tubular membrane was mainly around 20 Pa, but could be as high as about 40 Pa due to gas bubble movements. Nevertheless, a stable particle size distribution (PSD) for sludge particles was found at these shear stresses. It was, therefore, hypothesized that a high flux would be possible by applying biogas bubbles induced slug flow conditions in

tubular membranes whenever the filterability of the sludge could be improved, for example by the reduction of foulant concentrations through the addition of adsorbent or coagulant. Moreover, the observed stable sludge PSD, guarantees an acceptable level of sludge activity required for COD conversion.

Chapter 4 demonstrates that the addition of powdered activated carbon (PAC) enhanced the membrane fouling reduction effect of slug flow. However, the ability of the PAC to control fouling is limited and its removal leads to biomass loss. Hence, a new kind of adsorbent was clearly required that would, as far as possible, avoid biomass loss during adsorbent removal. A magnetic adsorbent with an approximate particle diameter of 1 μm was therefore manufactured and tested for fouling control in an anaerobic membrane bioreactor that was equipped with a side flow, inside-out, tubular ultra-filtration membrane and operated under slug flow conditions. Short-term experiments prior to adsorbent dosing showed that the applied slug flow enabled membrane operation at a flux in excess of 20 $L/m^2.h$, with a low rate of TMP increase. The magnetic adsorbent was added in an increasing concentration from 1 g/L to 5 g/L. However, the introduction of the magnetic adsorbent resulted in an increased TMP, even at the initial low concentration of 1 g/L. The rate of TMP increase was proportional to the concentration of adsorbent applied. Strikingly, addition of the adsorbent had no effect on sludge viscosity, although the filterability deteriorated significantly. Removal of the adsorbent from the sludge using an external magnetic field was unfortunately accompanied by significant biomass loss. It is therefore concluded that limited or no effective increase in membrane flux can be achieved by the addition of either PAC adsorbent or magnetic adsorbent.

Chapters 5 and 6 investigate the use of sodium chloride occurring naturally in wastewater, as a coagulant to control membrane fouling. Large quantities of sodium ions are present in saline wastewaters, providing the possibility of inducing coagulation through the use of a suitable shear gradient. Coagulation would be expected to reduce the number of the colloidal particles that are responsible for fouling in membranes. Shear-induced coagulation in saline waters was confirmed in this study, but this coagulation was unable to increase the membrane flux. There are two possible explanations for this result: (1) sodium ions may not act as a sufficiently strong coagulant for the saline sludge if the salinity of the saline sludge is not changed, so that the contribution of the salinity to membrane fouling reduction is inadequate, or (2) a low particle strength, attributed to the high salinity, may result in low sludge filterability.

Finally, a significant flux increase was achieved by the addition of a commercial aluminum coagulant, as described in Chapter 7. Results showed that an optimum coagulant dose (0.72 g Al/L) could significantly improve the membrane flux, from 10 to 50 $L/m^2.h$. The addition of the coagulant resulted in a slight decrease in sludge activity, whereas the average sludge particle size increased and the coagulant was detected on sludge-particle surfaces. These results indicate that dosing of coagulant could provide a possible means of controlling membrane fouling. Furthermore, the saline sludge activity could be increased from a low level, i.e. 0.4 g COD CH_4/g VSS.d, to a high level, exceeding 0.7 g COD CH_4/g VSS.d, through the addition of certain chemicals. Of the chemicals tested, glycine betaine and Ni^{2+} were found to increase saline sludge activity by almost 100 %, while K^+, Fe^{2+}, Co^{2+} either showed a less significant effect or had no effect on sludge activity (at the applied doses).

Contents

Chapter 1

Introduction

Chapter 1 Introduction

Water containing a significant quantity of salt (mostly NaCl) is termed saline. The presence of NaCl has a negative influence on the performance of biological wastewater treatment processes, and the sodium ion is considered to have the most significant impact. The extent of this influence depends on the degree of salinity. The term hypersaline is applied to a liquid with a salinity higher than that of the oceans. The successful treatment of saline and hypersaline wastewater is clearly important for the environment, but despite an estimated 5% of world's total industrial effluent being saline or hypersaline, little information is available on the biodegradation of organic pollutants under saline and hypersaline conditions, either by regular or halophilic microorganisms (Le Borgne et al. 2008).

Sodium chloride is widely used, not only for cooking and to melt snow and ice, but also in a wide variety of industries such as the manufacture of textiles, soap, glass, detergent, enamel, synthetic fibers, plastic, medicines, paper, and pesticides, as well as in dyeing, metallurgy, petroleum refining, and in the food industry (e.g., for sea food processing, milk processing, food canning, mustard making, casings fabrication, and as a result of acid-base neutralization in fermentation processes). Of the processing industries, seafood-processing operations produce wastewater containing substantial quantities of contaminants in terms of soluble and colloidal substances as well as high concentrations of nitrogen and suspended solids (Mines and Robertson 2003). The amount of wastewater discharged and the pollutant content of the wastewater obviously depend on the types of seafood and the processing technologies employed. The sodium chloride concentration in mustard tuber wastewater can be as high as 7% (w/v) (70 g NaCl/L) (Zhou et al. 2007), which is much higher than that of normal sea water, which is between 3.1-3.8%. Wastewater from the oil refining industry not only contains various kinds of complex chemical compounds, but the sodium chloride concentrations can range from that of fresh water to three times that of normal sea water (Diaz et al. 2002). Wastewaters from tanneries have a high content of organic matter and sodium chloride (Lefebvre and Moletta 2006, Mendoza-Roca et al. 2010).

The objective of this review is to summarize the available information concerning the influence that saline wastewater has on biological treatment processes, and to discuss the potential of anaerobic membrane bioprocesses in saline wastewater treatment. The related problem of possible serious membrane fouling, which can be promoted by saline conditions, is also discussed briefly, together with some important strategies for membrane fouling control.

1.1 Influence of salt on solute solubility

Inorganic ionic species can decrease the aqueous solubilities of nonpolar or weakly polar organic compounds. The magnitude of the effect depends on the compounds and the types of ions. An empirical formula has been established to describe the relationship between the solubility of a specific organic compound and salinity (Setschenow 1889):

$$\log\left(\frac{C_{iw}^{sat}}{C_{iw,salt}^{sat}}\right) = K_i^s[salt]_{tot} \qquad (1\text{-}1)$$

Where C_{iw}^{sat} is the saturation concentration of the organic compound in pure water (mol/L), $C_{iw,salt}^{sat}$ is the solubility of the organic compound in water under saline conditions (mol/L), K_i^s is the Setschenow or salting constant (mol/L), and $[salt]_{tot}$ is the total molar salt concentration (mol/L), which is the sum of various salt mole concentrations. The decrease in solubility can be attributed to the competition between non-polar or weakly polar solutes and dissolved ions for solvent molecules. Many environmentally relevant ions bind water molecules quite tightly in aqueous solutions, which disrupts the freedom of some water molecules to dissolve an organic molecule, and hence leads to either a decrease or an increase in solubility (Leberman and Soper 1995). Hence, it is expected that the loss of solubility of organic molecules has a (greater or lesser) negative influence on the biodegradation rates of organics, while the maximum substrate concentration is restrained by the decrease in solubility.

In addition to the effect that sodium chloride has on the solubility of organic solutes, when dissolved in water it also exerts an influence on the solubility of gases. The solubility of methane, carbon dioxide, hydrogen and oxygen all decrease as salinity increases. The decrease in solubility of oxygen makes the aerobic process more costly since aeration then requires a greater energy input. The solubilities of methane, hydrogen and carbon dioxide can be calculated using methods found in the published literature (Weiss 1974, Wiesenburg and Guinasso 1979). Calculations from these two references indicate that, when sodium concentration increases from 0 g/L to 100 g/L (NaCl), the solubilities (mmol/L) of carbon dioxide, methane, and hydrogen decrease in a linear manner from 26.43422, 0.78998, and 0.21095 to 26.42378, 0.78953 and 0.21086, respectively (temperature: 308 K). The slight solubility decrease of carbon dioxide, methane and hydrogen is not expected to influence biochemical reaction rates in the anaerobic conversion process. Alkalinity related to carbonate is also not significantly altered, due to the small variation in the solubility of carbon dioxide.

1.2 Influence of sodium chloride on microbial processes

1.2.1 Classification of halophilic and halotolerant microorganisms

Halotolerant microorganisms can survive in fresh water and tolerate certain concentrations of sodium chloride in water. Many microbial genera have specific requirements if they are to survive and function in such salty environments. For example, many halophilic bacteria require a high sodium concentration to maintain membrane integrity and therefore survive. Halophilic microorganisms can be roughly classified into three categories based on the most favorable sodium chloride concentrations for their maximum growth, as depicted in Table 1.1. Different units for NaCl concentration have been used in published literature rendering direct comparisons difficult, and hence different classifications of halophiles are given. Table 1.1 indicates that extreme halophiles can even live in environments in which the sodium chloride concentration is little less than the solubility of NaCl, which is more than 350 g/L. Slight halophiles live in environments in which the NaCl concentration ranges from 11.7 to 49.7 g/L, which corresponds to conductivities ranging from 18.3 to 77.7 mS/cm. However, microorganisms can survive in environments with very high salinity. The survival of microorganisms in a wide range of salinities offers opportunities for the biological treatment of wastewater, even under highly saline conditions.

Table 1.1 Classification of halophilic microorganisms based on NaCl requirement

Classification	Na^+ and NaCl concentrations			
	Na^+(mol/L)	Na^+(g/L)	NaCl (g/L)	NaCl (%)
slight halophiles	0.2-0.9	4.6-19.6	11.7-49.7	1%-5%
moderate halophiles	0.9-3.4	19.6-78.2	49.7-198.9	5%-20%
extreme halophiles	3.4-5.1	78.2-117.3	198.9-298.4	20%-30%

1.2.2 Mechanisms for microorganism adaptation to saline conditions

Negative influence of Na^+ on microorganisms

Each bacterial cell is enclosed by a semi permeable protoplasmic membrane that restricts the free movement of most ions and metabolites, but not of water (Ventosa et al. 1998). To prevent dehydration at high sodium concentrations, sodium is actively taken up by bacterial cells when salinity levels rise. However, sodium is toxic at high intracellular levels due to electrochemical and osmotic interactions with nucleic acids and proteins, and halophiles face the chronic challenge of preventing excess sodium from entering the cell (Valentine 2007). To achieve low intracellular Na^+ ion concentration against a constant influx of Na^+ ions leaking inside through a not completely impermeable membrane, two mechanisms of Na^+ extrusion can be employed: activity of Na^+/H^+ antiporter and presence of a primary respiration-driven Na^+ pump (Ventosa et al. 1998). Although Na^+ is required for the growth of halophilic microorganisms the concentration of Na^+ in a cell is generally lower than that in the surrounding medium (Ventosa et al. 1998). The differences in Na^+ concentrations can lead to osmotic pressure differences across cell membranes, as explained above. If the TMP is not balanced, water in the cell body will leak out, which will affect the activity of the cell.

Adaptation strategies

Halophilic bacteria and archaea can accommodate fluctuations in external osmotic pressure and maintain an osmotic balance between their protoplasms and a hypersaline extracellular environment by one of two methods, known as the 'salt in' strategy and the 'salt out' strategy. The former involves K^+, as well as Na^+, accumulating in the cell body to balance pressure differences across the cell membrane, while the latter uses uncharged and highly water-soluble organic solutes to prevent microorganisms from suffering damage due to osmotic pressure difference. Halophilic archaea use the 'salt in' strategy whereas halophilic bacteria employ the 'salt out' strategy (Le Borgne et al. 2008). The intracellular salt concentrations of halophilic or halotolerant eubacteria are low, and they maintain an osmotic balance between their cytoplasm and the external medium by the 'salt out' strategy (Detkova and Pusheva 2006, Margesin and Schinner 2001).

'Salt in' strategy

Extreme halophiles accumulate enormous quantities of potassium in order to remain hypertonic to their environment; the internal potassium concentrations may reach 4 to 7 mol/L. In fact, high levels of potassium are required to stabilize the halophilic enzymes. The mechanism of osmoregulation requires special adaptation of the intracellular enzymatic machinery, which has to be operative in the presence of high sodium chloride concentrations (Oren et al. 1992). This 'salt in' strategy turns out to be remarkably effective for colonizing of habitats with permanent high salinities, but is far less useful in coping with habitats of moderate salinity or environments that experience drastic fluctuations in their osmotic conditions (Ventosa et al. 1998).

'Salt out' strategy

Compatible solutes are solutes that do not interfere with the bacterial metabolism and growth when present at high intracellular concentrations. Compatible solutes are charged organic compounds that may accumulate to high concentrations, keeping intracellular monovalent cations at low levels. Because the 'salt out' adaptation mechanism does not require evolutionary adaptation of proteins and cellular processes to high sodium chloride concentrations, this response to osmotic stress is prevalent not only in bacteria, but also in fungal, plant, animal, and human cells (Martin et al. 1999). In any case, uptake of external osmolytes in the medium is preferred over synthesis de novo (Ventosa et al. 1998). Many methanogens can synthesize glycine betaine. Yerkes et al. (1997) found that concentrations of betaine as low as 1 mmol/L were effective in reducing the toxicity symptoms due to high concentrations of sodium in an anaerobic reactor system, as indicated by a significant reduction in the methanogenesis lag time (Yerkes et al. 1997).

1.3 Effect of Na^+ on sludge properties

High salt concentrations significantly reduce the treatment efficiency of anaerobic processes under mesophilic and thermophilic conditions (Guerrero et al. 1997, Vallero et al. 2003a, Vallero et al. 2003b, Vallero et al. 2004), which can be due to a direct toxic effect of the salts that lead to biomass wash-out due to salt induced disintegration of flocs and granules (Pevere et al. 2007). The presence of Ca^{2+}, even at low concentrations (100-200 mg/L), strongly enhances the rate of anaerobic sludge granulation at (Liu et al. 2002, Mahoney et al. 1987) and increases the strength of anaerobic granular sludge (Teo et al. 2000). Likely, bioflocculation is promoted because divalent cations can bridge negatively charged functional groups of EPS. The promoted bioflocculation finally contributes to aggregation and stabilization of the matrix of biopolymers and microbes, which prevents the wash out of biomass from bioreactors (Pevere et al. 2007, Sobeck and Higgins 2002).

In addition, the presence of fine particles (0-50 µm) in an anaerobic granular suspension is slightly modified by Na^+ addition but strongly modified by Ca^{2+} addition (Pevere et al. 2007). Similar to the observations made under anaerobic conditions also under aerobic conditions monovalent and divalent cations generally play different roles in affecting the settling and dewatering properties of activated sludge. It was claimed that the influence was caused not only by physical/chemical factors but also by physiological factors (Novak et al. 1998).

1.4 Treatment of saline wastewaters by conventional techniques

1.4.1 Aerobic bioprocesses

Various investigations have been conducted into saline wastewater treatment under aerobic conditions, involving various different techniques and types of saline wastewaters. Halophilic or halotolerant inoculums were involved in most of such aerobic research, in which sodium chloride concentrations ranged from 10 g/L to 150 g/L (Abou-Elela et al. 2010, Dan et al. 2002, Dincer and Kargi 2001, Gharsallah et al. 2002, Kargi and Dincer 1997, Kargi et al. 2000, Kubo et al. 2001, Lefebvre et al. 2004, Lefebvre et al. 2005, Moon et al. 2003, Uygur and Kargi 2004, Woolard and Irvine 1994). Fed-batch reactors, rotating biodiscs, and sequencing batch operations were used to retain biomass in bioreactors, as well as membranes. Antileo et al. (1997) reported that COD removal efficiency decreased when rotating biodiscs were used to treat molasse wastewater in which the sodium chloride concentration increased from 50 g/L to 100 g/L . They suggested that efficient sludge retention and sufficient adaptation time can lead to good pollutant removal efficiencies. Aloui et al. (2009) found that an acclimatized consortium can be efficient for the treatment of fish processing saline wastewaters, even in the presence of sodium chloride concentrations of up to 40 g/L, although inhibition was found to be significant for sodium chloride concentrations exceeding 40 g/L. A technology based on aerobic granular sludge has been developed by Figueroa et al. (2008) for the treatment of saline wastewater. It was found that aerobic granular sludge was able to completely remove organic matter in an sequential biological reactor (SBR) that was used to treat fish canning effluent at an NaCl concentration of 30 g/L (Figueroa et al. 2008). However, the efficiency of ammonia removal was not satisfactory.

1.4.2 Anaerobic bioprocesses

Influence of saline conditions on methanogenesis

The presence of salt may alter the biodegradation rates of pollutants in water. Not all biological degradation processes known to function in fresh water environments have been shown to also be operative in the presence of high sodium chloride concentrations (Oren et al. 1992). For example, no significant breakdown of long-chain straight hydrocarbons such as hexadecane could be demonstrated in Great Salt Lake brines at salinities exceeding 20% (200 g NaCl/L) (Ward and Brock 1978). However, reductive dechlorination of chlorophenols and chlorophenoxyphenols, and reduction of nitro-substituted aromatic compounds to corresponding amino derivatives, are possible under anaerobic saline conditions (Oren et al. 1992, Oren et al. 1991). Methanogenesis from simple compounds such asH_2/CO_2 and formate, proceeds quite well at high salinity (Detkova and Pusheva 2006). However, the degradation of volatile fatty acids (VFA), and particularly propionic acid, seems to be more problematic, since it is the main accumulating intermediate compound found in an anaerobic process inhibited by salt (Gebauer 2004).

Methanogenesis remains an important process in marine and hypersaline environments where certain carbon sources are available that cannot be used by sulfate reducers (Oremland et al. 1982). These carbon sources include methanol, dimethylsulfide, and methylated amines. At high sodium chloride concentrations, the most important methanogenic precursors are not hydrogen/CO_2 or acetate, but more specific substrates such as methanol, methylamines and methionine (Oren 1988), which attributes to the fact that at high salinity levels, non-competitive substrates such as trimethylamine or dimethylsulfide can be more important as precursors of methane. Apparently, aceticlastic and hydrogenotrophic methanogens are more susceptible to salt than methylotrophic methanogens. In fact, methylotrophic methanogens are nearly always the dominant methanogens under hypersaline conditions. Methylamines are probably the main carbon and energy sources for halophilic methanogens.

Influence of salt on anaerobic granulation

The granulation of anaerobic sludge plays an important role in wastewater treatment. The presence of multivalent ions can promote the formation of anaerobic granules, which can be attributed to a higher degree of flocculation and charge neutralization. The addition of ferrous iron has been reported to increase the mean sludge granule diameter and induce a stable and excellent COD conversion rate (Vlyssides et al. 2009). Similarly, other researchers have demonstrated that the addition of $AlCl_3$ enhances the sludge granulation process in an upflow anaerobic sludge blanket (UASB) reactor (Yu et al. 2001). In addition, a high calcium concentration results in a rapid formation of dense granules (van Langerak et al. 2000).

According to the DLVO theory, positively charged ions can reduce the repulsive energy barrier between negatively charged fine particles, which accelerates the aggregation of particles and the formation of larger particles. It could therefore be hypothesized that an increase in Na^+ will lead to a larger mean granule size. However, when a large quantity of Na^+, rather than Ca^{2+}, Al^{3+} and Fe^{3+} , is present, the situation changes. Ismail et al. (2008) reported a sharp drop in granule strength as a result of high Na^+ concentrations (Ismail et al. 2008). Batch tests showed that sodium in high concentrations seems to displace the calcium from granular sludge, a factor known to affect anaerobic granules formation (Jeison et al. 2008a), which may partially explain why Na^+ reduces granular strength. Another reason may relate to the EPS that is excreted by microorganisms, which plays a key role in aggregating microorganisms to form activated sludge (Liao et al. 2001, Wilen et al. 2003), since the properties of EPS can be influenced by salinity. The treatment of highly saline wastewater, therefore, requires an excellent sludge retention capacity since the smaller sludge particles can easily be lost from conventional reactors.

Performance of anaerobic bioprocesses

In addition to the use of aerobic processes, anaerobic saline wastewater treatment has intrinsic advantages, particularly when treating highly concentrated organically polluted wastewaters. The sodium chloride concentrations of saline wastewater treated by anaerobic processes in these investigations ranges from 10 g/L to 70 g/L and are lower than those investigated in the aerobic processes (Aspe et al. 1997, Boardman et al. 1995, Gebauer 2004, Guerrero et al. 1997, Habets et al. 1997, Lefebvre et al. 2006, Mosquera-Corral et al. 2001, Omil et al. 1995, Rovirosa et al. 2004, Vidal et al. 1997). Many types of reactors have been tested as well as different kinds of wastewater. Continuous stirred tank reactor (CSTR) was used to treat wastewater from a fish farm and a fishery (Aspe et al. 1997, Gebauer 2004), but COD removal efficiencies were only about 50%. Contact systems and biofilm technologies such as a fixed bed anaerobic filter reactor were used to retain the biomass, which led to higher COD removal efficiencies (Guerrero et al. 1997, Omil et al. 1995, Rovirosa et al. 2004, Vidal et al. 1997). However, an increase in sodium chloride concentration was found to lead to lower COD removal efficiency (Kapdan and Boylan 2009). When inhibition of the anaerobic process was observed, propionic acid was found to be the main VFA (Gebauer 2004). Although aerobic granular sludge was successfully formed in aerobic reactors, stable granular sludge could not be maintained in a UASB bioreactor treating tannery soak liquor (Lefebvre et al. 2006). Hence, the COD removal efficiency could be as high as 78% at the cost of a low organic load of only 0.5 kg COD /$m^3 \cdot d$ at 71 g NaCl/L (Lefebvre et al. 2006). Inhibition of methanogenesis was also found to occur when the concentration of Na^+ was above 5.25 g/L in a UASB bioreactor treating inuline industry effluent (Boardman et al. 1995).

In view of the poor performance of anaerobic bioreactors, compatible solutes have been added into such bioreactors to help the anaerobic biomass cope with saline conditions (Vyrides and Stuckey 2009a, Yerkes et al. 1997). The used compatible solutes consist of amino acids, ectoines, polyols, betaines, etc. They have been demonstrated to be effective in shortening the lag time for methanogenesis in anaerobic sludge under saline conditions (Yerkes et al. 1997). All the compatible solutes were found to alleviate sodium inhibition, although glycine betaine was the most effective (Vyrides and Stuckey 2009a, Yerkes et al. 1997).

1.4.3 Drawbacks of conventional techniques

Most research into anaerobic saline wastewater treatment using conventional methods has been confined to laboratories. Bioprocesses with efficient sludge retention capacities were generally found to give better pollutant removal efficiency, and an increase in salinity undoubtedly decreases COD removal efficiency.

Non-halophilic and non-halotolerant microorganisms are not able to efficiently remove organic pollutants under high sodium chloride concentrations and their capacity for adaptation to salinity is easily lost after exposure to low salinity conditions. Kargi and Dincer summarized the problems affecting the biological treatment of saline wastewater under four categories (Kargi and Dincer 1996):

- A limited extent of adaptation. Conventional cultures cannot be used to effectively treat saline wastewaters with a sodium chloride content greater than about 3% (30 g/L).
- Sensitivity to variations in ionic strength. A shift in sodium chloride concentration from 0.5% to 2% typically causes significant reductions in system performance. Rapid change in sodium chloride concentration causes more adverse effects than gradual change. Equalization to constant sodium chloride concentration is essential before treating saline wastewater.
- Reduced degradation kinetics. Biological degradation rates for organic compounds decrease as sodium chloride concentration increases. Saline wastewaters, therefore, need to be treated at low organic loading rates.
- High suspended solids concentration in effluent. Sodium chloride in wastewater increases buoyancy, thereby causing low sedimentation efficiency.

The efficiency of biological wastewater treatment clearly depends on the presence of appropriate microorganisms, their concentrations, and hydraulic retention time. Furthermore, the efficiency of biological saline wastewater treatment is dependent on the sodium chloride concentration, the type of pollutant, the organic load, the degree of aeration in case of aerobic treatment, and whether microorganisms in the bioreactor have adapted to the wastewater. Changes in salinity have been found to have a greater effect on the removal of organic matter than changes in hydraulic retention time or the organic loading rate (Lefebvre et al. 2005).

1.5 Potential of membrane processes for the treatment of saline wastewater

1.5.1 Performance of membrane processes

Biofilm reactors are useful in terms of realizing good biomass retention that is required for successful biological treatment of wastewater. However, the formation of biofilm at different salinities (and especially at high salinities) is problematic, as indicated by unstable granulation in UASB reactors under saline conditions (Lefebvre et al. 2006) and unstable biofilm formation in anaerobic filters (Guerrero et al. 1997).

In contrast, the use of a membrane bioreactor (MBR) offers a promising solution to these problems (Section 1.4.3). First, biomass will be efficiently retained by membrane separation, irrespective the physiological adherence properties of the microorganisms. Second, the retained biomass can adapt to the high salinity conditions, e.g. by the growth of halotolerant and/or halophilic microorganism, possibly able to tolerate a wide salinity range. Vyrides and Stuckey (2009a) have shown that adapted microorganisms are able to survive in environments with a wide range of sodium chloride concentrations. In addition, the applied hydraulic retention time (HRT) may combat fluctuations in the influent sodium chloride concentration. Moreover, the high possible TSS concentration that results from membrane retention may facilitate the application of high volumetric loads and thus compensates for reduced degradation kinetics. Finally, effluents from MBR systems are characterized by negligible suspended solids concentrations. The above discussion clearly indicates that MBRs offer interesting perspectives for saline wastewater treatment.

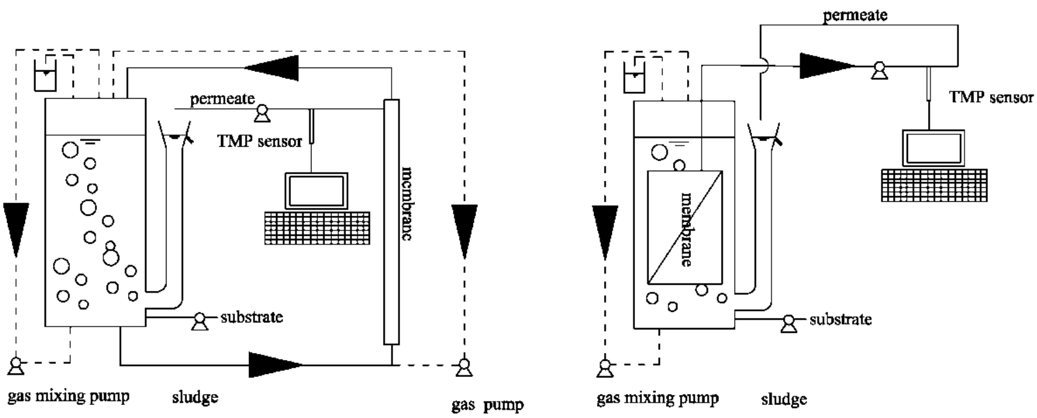

Figure 1.1 Suggested configurations of AnMBR
Left: cross flow type; right: submerged type

Little research has been reported to date on the use of aerobic MBRs for saline wastewater treatment (see e.g. review by Lay et al. 2010). A hybrid membrane bioreactor was used to treat wastewater from a fish canning factory with a sodium chloride concentration of up to 84 g/L (Artiga et al. 2008). A COD removal efficiency of 92% was obtained after the sludge had adapted to the salinity. Sharrer et al. (2007) achieved a COD removal rate exceeding 99% at a sodium chloride concentration of 32 g/L, applying an organic load of 0.55 g COD/g VSS.d. Similar high COD removal efficiencies have also been reported by other researchers (Reid et al. 2006, Tam et al. 2006).

Some configurations of AnMBRs are illustrated in Figure 1.1. Anaerobic MBRs have been tested for the treatment of many different kinds of wastewater, including wastewater from coke (Zhao et al. 2009, Zhao et al. 2010), municipal solid waste leachate (Trzcinski and Stuckey), municipal wastewater (Herrera et al. 2010, Ho and Sung 2009, Zhidong et al. 2009), azo dye (You and Teng 2009), hydrogen production (Lee et al. 2009, Lee et al. 2007), acidified wastewater (Jeison et al. 2008b), particulate organic matter (Jeison et al. 2008c), landfill leachate (Bohdziewicz et al. 2008, Xu et al. 2008), cheese whey (Saddoud et al. 2007), slaughterhouse wastewater (Saddoud and Sayadi 2007), and food wastewater (He et al. 2005), kraft evaporator condensate treatment (Gao et al. 2011, Xie et al. 2010). However, little research has been found into the use of membrane bioreactors for anaerobic treatment of saline wastewater (Jeison et al. 2008b, Vyrides and Stuckey 2009b). Research to date into the use of membrane bioprocesses for treatment of saline wastewater is summarized in Table 1.2. The experiments of both Jeison et al. (2008b) and Vyrides and Stuckey (2009b) were conducted in lab scale using synthetic wastewaters. Membranes not only retained sludge effectively in their bioreactors, but also prevented macromolecules from being washed out from the bioreactors, which improved the reduction of effluent COD. L Vyrides and Stuckey (2009b) reported 99% removal of COD, even when the salinity was 35 g/L.

Table 1.2 Membrane processes for saline/hypersaline wastewater treatment

Wastewater source	C_{NaCl} g/L	Organic load gCOD/gVSS.d	HRT h	Removal %	Flux L/m^2h	Operation
Fish canning factory	84	0.35	120	92(oxic/aerobic)	4.6	immersed
Fish canning factory	32	0.48	120	99(oxic/aerobic)	27.8	cross flow
Aquaculture system	32	0.55	40.8	>99(oxic/aerobic)	7.1	immersed
Synthetic	32	0.3	36	85(aerobic)	3.7	immersed
Synthetic	32	0.19	17	91(aerobic)	1.9	immersed
Synthetic	0-35	----	8-20	99(anaerobic)	8	immersed
Synthetic	65	0.4	20	70(anaerobic)	15	cross flow

References (Artiga et al. 2008, Dan et al. 2002, Jeison et al. 2008b, Sharrer et al. 2007, Vyrides and Stuckey 2009b)

From Table 1.2 it is clear that membrane processes generally offer higher COD removal efficiency than the conventional technologies. Although membrane flux depends on many factors, membranes operated in immersed mode gave very low fluxes, whereas those in cross flow mode gave higher fluxes, which may be more desirable in terms of reducing operation costs. It should be emphasized, however, that research into the use of membrane-assisted bioprocesses for saline wastewater treatment is still very limited. More research is required into the feasibility of their use for industrial applications.

1.5.2 Advantages of anaerobic MBRs over aerobic MBRs

The kinetics of substrate degradation in bioreactors can be simply described in the form of the following equation:

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \frac{\mu_m XS}{\mathrm{Y}(K_s + S)} \qquad (1\text{-}2)$$

Where: S: substrate concentration in bioreactor, kg COD/m^3; Y: yield coefficient; μ_m: maximum specific growth rate, kg COD substrate/(kg COD biomass.d); K_s: half saturation coefficient, kg COD substrate/(kg COD biomass); X: biomass, kg COD/m^3.

The above equation shows that a high biomass concentration and a low half saturation coefficient contribute to a high substrate removal rate. The application of membranes could completely retain biomass in reactors and therefore high biomass concentrations can be obtained. The retention of biomass (X) offers a fundamental condition for a further increase in the efficiency of the reactors by increasing the volumetric bulk sludge activity. The further increase in sludge activity could be achieved by the application of compatible solutes or potassium ions (see sections regarding ‘salt in’ and ‘salt out’). Therefore, it is considered that AnMBR would possess a good potential to treat saline wastewater with high organic strength.

Anaerobic MBRs appear to offer a powerful solution for saline industrial wastewater treatment, especially at very high salt concentrations. Moreover, because anaerobic processes proceed without oxygen it is not necessary to consider the problem of oxygen transfer under saline conditions, which not only saves the energy that would be required for aeration but also allows much higher concentrations of (anaerobic) biomass. In addition, methane can be generated during anaerobic processes and can be used as an energy source, thus further decreasing the operating costs. Although the anaerobic granular sludge process is successfully and wildly applied by taking 89% of the market of anaerobic processes (van Lier 2008), granulation faces problems under saline conditions. There is also evidence in the literature that anaerobic membrane bioreactors show advantages over sludge bed reactors in terms of recovering from propionate intoxication (Jeison 2007b). In fact, the contrary has been postulated by Brockman and Seyfried owing to the fact that the high shear forces in anaerobic membrane bioreactors disturb the juxtaposition of propionate oxidizers and hydrogenotrophic methanogens, a pre-requisite for efficient propionate oxidation under anaerobic conditions (Brockmann and Seyfried 1996, Stroot et al. 2001). Perfect sludge retention capability and thus infinite solids retention times also offers a high potential for pollutant removal. In addition, effluent from a membrane bioreactor may be suitable for further treatment such as reverse osmosis, in order to allow its reuse.

1.6 Research needs and opportunities

In order to increase the feasibility of AnMBR on saline wastewater treatment, attentions should be paid to increase sludge activity and control membrane fouling. The two aspects are discussed below.

1.6.1 Aspect of bioprocess

There are many kinds of saline wastewaters that have not been treated by AnMBR. In addition, studies using AnMBR on the treatment of saline wastewaters are mainly limited to lab scale. Pilot or full-scale studies should be undertaken to further confirmation of the feasibility of AnMBR for saline wastewater treatment.

Furthermore, as stated above, sodium toxicity inhibits sludge activity. However, the application of compatible solutes and potassium could be used to increase the sludge activity. Presently, it is not known what dosages of compatible solute and potassium should be applied under different salinity conditions and what level of sludge activity could be achieved at the applied dosages. Further, the fates of these applied chemicals should be studied in order to obtain a more scientifically satisfying dosing strategy.

An additional effect of the application of compatible solute and potassium might be that the excretion of EPS and the strength of anaerobic sludge particles would be affected. The amount and property of EPS would be influenced upon the addition of compatible solute and potassium, which could have an impact on sludge biogranulation and finally have a direct impact on membrane fouling. In addition, the change in strength of sludge would also change sludge PSD under applied shear conditions, which could also have an impact on sludge filterability. The membrane fouling of AnMBR is further discussed below.

1.6.2 Aspect of membrane fouling

Membrane fouling in AnMBR

The main challenge in combining membrane separation with bioprocesses lies in controlling membrane fouling. The membrane fluxes in saline aerobic MBRs are lower than 10 L/m^2.h (Lay et al. 2010). High concentrations of dissolved oxygen lead to better sludge filterability, which is attributed to greater particle size and higher porosity in the cake layer (Kang et al. 2003). The flux in anaerobic MBRs, in which no free oxygen exists, is generally lower than that in aerobic MBRs. Increasing the flux of an anaerobic MBR not only enhances its applicability to saline wastewater treatment but can also pave the way for other applications.

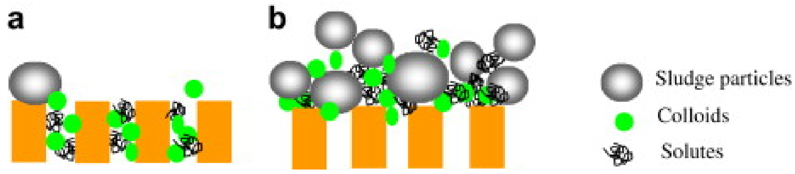

Figure 1.2 Membrane fouling process in MBRs: (a) pore blocking and (b) cake layer (Meng et al. 2009)

It is claimed that the cake layer formed at the membrane surface is responsible for the increased membrane filtration resistance in long term operations of AnMBR (Jeison 2007a). Figure 1.2 shows the main components of foulants in aerobic MBR and AnMBR. Soluble microbial products (SMPs) and colloids have been identified by many researchers as major foulants of membranes (Faibish et al. 1998, Jarusutthirak and Amy 2006, Jarusutthirak et al. 2002, Liang et al. 2007, Rosenberger et al. 2006, Vrijenhoek et al. 2001). Inorganic fouling has also been reported, in addition to organic fouling. The formation of struvite on membrane surfaces (Kim et al. 2007) and the accumulation of cations such as Ca^{2+} and Mg^{2+} lead to a compact fouling layer (Tam et al. 2006). Sodium ions are also reported to suppress the electric double layer of colloids, again leading to the formation of a compact fouling layer on a membrane surface (Tam et al. 2006). However, this observation contradicts those made by Lee (Lee and Elimelech 2007), who used water with a high sodium concentration to back-flush a fouled membrane and found that saline water had a better cleaning effect than fresh water.

Discussion about membrane fouling control

Many methods of controlling membrane fouling in both anaerobic and aerobic MBRs have been investigated by numerous researchers. Some major applied methods are listed in Table 1.3 and will be briefly discussed below. Detailed reviews of these methods have been previously published (Hilal et al. 2005, Huang et al. 2009, Liao et al. 2006, Wakeman and Williams 2002), and will therefore not be provided in this chapter. The possible methods investigated for controlling foulant accumulation on a membrane surface operated in one of three ways: (1) by reducing the concentration of the foulant, (2) by promoting mass transfer at the membrane surface, or (3) by reducing the capacity of the foulant to attach to the membrane surface.

Table 1.3 Mainly applied methods to control membrane fouling in AnMBR

Methods	Comments	References
Activated carbon	Should be an optimum dose	Akram and Stuckey 2008, Hu and Stuckey 2007, Park et al. 1999, Vyrides and Stuckey 2009b
Gas sparge	Helpful	Jeison and van Lier 2008, Martinez-Sosa et al. 2011
Chemical cleaning	Irreversible fouling still could be observed	Herrera-Robledo et al. 2011, Zhang et al. 2007
Physical cleaning	Fully recover membrane flux	Martinez-Sosa et al. 2011
Control struvite formation	Useful for ceramic membrane, not for polymeric membrane	Kim et al. 2007
Ultrasonic cleaning	Effective in a long term operation	Xu et al. 2010
Coagulant	Should be an optimum dose	Wu et al. 2009, Xing et al. 2010

1) Reducing foulant concentration

The addition of coagulants is known to promote the aggregation of fine particles such as colloids, resulting in the formation of larger particles. The coagulation effect depends on the type of coagulant used, the dose, and the degree of mixing. An overdose of coagulant will lead to the re-stabilization of fine particles. Although good fouling control has been shown to be achievable through the use of coagulants, the in-line addition of coagulant in AnMBRs for increasing sludge filterability has not been fully investigated. The addition of coagulants did not show any toxic effect on aerobic microorganisms (Iversen et al. 2008) but it remains unclear whether coagulation would negatively influence the activity of anaerobic microorganisms. In addition, the fate of the coagulants used in these studies is also not clear.

Apart from adding coagulants, the addition of an adsorbent can also be useful in combating membrane fouling. The adsorbent favored by most researchers is PAC (Akram and Stuckey 2008, Hu and Stuckey 2007, Park et al. 1999, Vyrides and Stuckey 2009b). Because of its large surface to volume ratio, PAC tends to adsorb material to its surface in order to balance its unsaturated force field, thus providing its adsorption capacity. PAC can alleviate membrane fouling by reducing the amount of SMP in the sludge, leading to a lower fouling rate. However, overdoses of PAC (3.4 g/L) has been shown to make membranes less permeable (Akram and Stuckey 2008) although Park et al reported that adding a higher dose of PAC (5 g/L) did not foul their membrane (Park et al. 1999). In addition, once the PAC has reached its adsorption capacity it is incapable of any further adsorption. Since foulants such as SMP are generated continuously in reactors, PAC would require continuous addition and removal, which might not be practical in an anaerobic MBR since it is a closed system with very long solids retention times (in dependence of the substrate). The removal of PAC could lead to a gradual loss of anaerobic biomass.

The salt in wastewater may play a role in the control of membrane fouling by suppressing the zeta potential of fine particles. In the presence of suitable mixing, this decrease in zeta potential may result in a significant flocculation effect, which can reduce the number of fine particles and thus reduce membrane fouling. However, the reduction in zeta potential may also decrease the porosity of the cake layer, which is a negative effect. Whether salt can be used to control membrane fouling through suitable mixing in the treatment of saline wastewater by membrane processes, therefore, remains unclear.

2) Promoting mass transfer at membrane surfaces

An alternative to reducing the concentration of foulant in the bulk solution is to promote mass transfer from the membrane surface to the bulk solution, in order to prevent the accumulation of foulant.

Some researchers have attempted to introduce turbulence promoters in tubular membrane modules, and significant flux improvement has been reported as a result (Krstic et al. 2002, Mameri et al. 1999, Pal et al. 2008, Xu et al. 2003). Some membrane systems use two-phase flow to overcome concentration polarization and membrane fouling. The most likely flow patterns are bubble flow and slug–flow due to the relatively low gas flow rates applied (Cui et al. 2003). Turbulence promoters and slug flow combat membrane fouling by increasing shear stress or turbulence at the membrane surface. However, the increase in shear stress may harm the biological performance of bioreactors, especially anaerobic bioreactors because the shear stress may break the juxtaposition of H_2 producers and H_2 scavengers and therefore influence inter-species hydrogen transfer. A dense sludge structure makes efficient inter-species hydrogen transfer possible between microbial consortia, and damage to sludge particles may have the undesirable effect of impeding inter-species hydrogen transfer.

3) Reducing foulant's capacity to attach to membrane surfaces

Membrane characteristics such as pore size, porosity, surface charge, roughness and hydrophilicity, etc., have been proven to have an impact on membrane performance (Meng et al. 2009). Hydrophilic membranes have better antifouling properties than hydrophobic membranes (van der Marel et al. 2010). For example, a polyacrylonitrile membrane was found to be more resistant to fouling than PVDF and polyethersulfone membranes (Zhang et al. 2008). Much attention has therefore been given to increasing the hydrophility of membranes by membrane modification (Hashim et al. 2009, Oh et al. 2009, Wang et al. 2009). Moreover, predictions show that the repulsive interaction energy barrier between a colloidal particle and a rough membrane is lower than the corresponding barrier for a smooth membrane (Hoek et al. 2003). Also, a narrow pore size is favorable for membrane fouling reduction (Meng et al. 2009). The aim of changing the properties of the membrane is, at least partially, to alter the ability of foulants to attach to the membrane surface, which, even if foulants have accumulated on the membrane surface, makes it, more easily washed away.

As to the influence of salinity on the surface property of membranes, it is found that salt may make cationic surfactant coated membranes more hydrophilic, as evidenced by a contact angle reduction (Kim et al. 2009). Therefore, salt in water may contribute to reduce membrane fouling in wastewater treatment if a cationic surfactant coated membrane is applied.

1.7 Scope and outline of this thesis

The main purpose of this thesis is to increase the membrane flux of anaerobic membrane bioreactors, with a focus on the treatment of saline wastewaters. Two main steps were applied to achieve a high flux: 1) managing shear stress at the membrane surface in order to enhance the back transport of foulants from the membrane surface to the sludge bulk solution, and 2) improving sludge filterability.

During the application of the first method, slug flow and inserts were used in order to induce pulse shear stress in a tubular membrane, which provides the contents of chapter 2. Then, in order to clarify the role of shear stress in membrane fouling control, a computational fluid dynamic (CFD) model was developed. Chapter 3 presents the results supplied by the model.

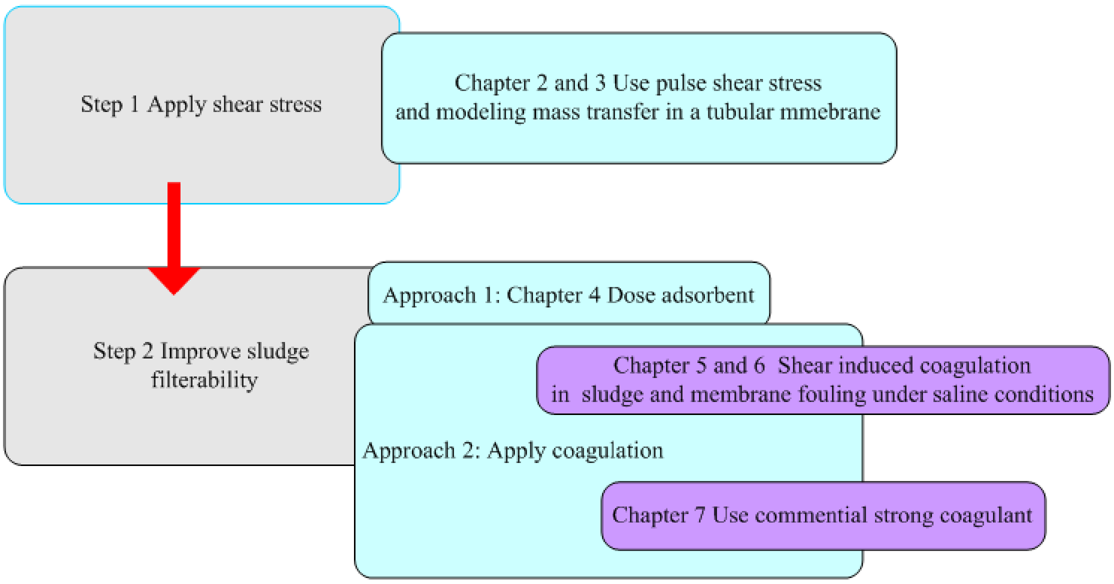

Figure 1.3 Structure of the thesis

By using the results in chapter 2 and 3 as a basis, reducing the concentration of foulant with a precondition that reactor operation is not disturbed is the other major content of this thesis. Adsorption and coagulation were the two approaches applied to reduce the foulant concentration. Chapter 4 is about the application of adsorbent and the discussion of the application of it. As for the coagulation, two kinds of coagulant were applied. Sodium ion, present in saline wastewater, was tested as a coagulant to induce coagulation in saline wastewaters. A basic study and the effect of using sodium ion as a coagulant to control fouling are the contents of chapter 5 and 6. Finally, chapter 7 describes results of using aluminum hydroxyl chloride coagulant (CAS：12042-91-0) to significantly increase membrane flux.

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Chapter 2

Pulse shear stress for anaerobic membrane bioreactor fouling control

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Abstract
Increase in shear stress at membrane surfaces is a generally applied strategy to minimize membrane fouling. It has been reported that a two-phase flow, better known as slug flow, is an effective way to increase shear stress. Hence, slug flow was introduced into an anaerobic membrane bioreactor for membrane fouling control. Anaerobic suspended sludge was cultured in an anaerobic membrane bioreactor (AnMBR) operated with a side stream inside-out tubular membrane unit applying sustainable flux flow regimes. The averaged particle diameter decreased from 20 µm to 5 µm during operation of the AnMBR. The standard deviation of the particle diameter measurement was 1 µm. However, the COD removal efficiency did not show any significant deterioration, whereas the SMA increased from 0.16 to 0.41 g COD/gVSS.d, with a standard deviation of 0.03 g COD/gVSS.d. Nevertheless, the imposed gas slug appeared to be insufficient for adequate fouling control, resulting in rapidly increasing trans-membrane pressures (TMP) operating at a flux exceeding 16 $L/m^2.h$. The tubular membrane was subsequently equipped with inert inserts for creating a locally increased shear stress for enhanced fouling control. Results show an increase in the membrane flux from 16 $L/m^2.h$ to 34 $L/m^2.h$ after the inserts were mounted in the membrane tube.

2.1 Introduction

Induced surface shear is considered to be a major strategy to control membrane fouling (Cui et al. 2003). It is reported that the cake resistance is the predominant resistance, which can be minimized by increasing the membrane surface shear stress (Su et al. 2008). This finding is also evidenced by other authors (Elmaleh and Abdelmoumni 1997, Karasu et al. 2009).

Although application of a high shear stress is a widely accepted approach to alleviate membrane fouling, it is likely that the applied shear stress negatively impacts the microbial activity, resulting in a decreased performance of the membrane bioreactor. It is reported that a high shear stress decreases sludge activity in an aerobic MBR (Khan 2008, Kim 2001). In addition, the negative impact was also reported in an anaerobic MBR (Jeison 2007).

In addition, the response of cells to fluid mechanical shear stress varies with cell type and depends on their physiological characteristics, culture conditions, and previous history of growth among others (Joshi et al. 1996). Thus, working with a bioreactor, different reactor operational conditions, such as impeller mixing, will have an impact on bioreactor performance (Zhang et al. 2010, Zhong 2010).

The generally observed high SMA of anaerobic granular sludge originates from the high density of methanogenic bacteria and the fact that micro-colonies of acetogenic bacteria are closely linked with micro-colonies of hydrogenotrophic methanogenic archaea in so-called syntrophic associations, which allows an efficient interspecies hydrogen transfer (Hulshoff Pol et al. 2004). A high shear stress could possibly disrupt these syntrophic aggregates, creating suspended biomass and therefore leading to a decreased anaerobic sludge activity. However, high shear, though it does harm to sludge activity, is required to minimize membrane fouling. Therefore, a gentle shear, which is high enough to provide shear, but low enough to secure sludge activity, is proposed in systems that combine biological activity with membrane separation processes.

Gas slug (Taylor bubble) is perceived a useful technique to increase shear stress near the membrane surface for achieving a high flux. However, the impact of the Taylor bubble generated shear stress on sludge activity is not yet known. Moreover, in the current research, the sustainable flux flow region was selected for the cross flow AnMBR operation. Our present experiments focus on impact of pulse shear invoked by Taylor bubbles on membrane fouling and the specific methanogenic activity.

In addition, alternative to the Taylor bubble approach, inserts were mounted in a tubular membrane to locally increase the shear stress. Although various authors confirmed the positive effect of such inserts (Krsti et al. 2002, Mameri et al. 1999, Pal et al. 2008, Xu et al. 2003), this method has yet not been tried in anaerobic MBRs. Therefore, several experiments were performed to evaluate the potential of pulse shear invoked by fixed inserts on membrane fouling control.

2.2 Materials and methods

A cross flow anaerobic MBR was operated using a ultra-filtration (UF) membrane module in gas-lift mode. A tubular PVDF membrane (Norit, the Netherlands) was employed (30 nm pore size). The inner diameter and length were 5.2 mm and 0.74 m, respectively. A cylindrical vessel was used as anaerobic bioreactor with an effective volume and inner diameter of 4.5 L and 10 cm, respectively. Temperature of the bioreactor was kept at 35 ^{0}C by means of a water jacket surrounding the bioreactor. A pump (Watson Marlow 323D) was also used for pumping supernatant into the tubular membrane in which, during some experiments, inserts were placed. Other three pumps (Watson Marlow 323D) were used for mixing the reactor (gas mixing), permeation extraction, and substrate supply. Schematic graphs of the experimental setup and the inert inserts are shown in Figure 2.1and Fig. 2.2, respectively. When the membrane was operated in a gas lift mode, the setup was identical to the one depicted in Figure 1.1 (left). Gas lift operation mode lasted during most of the experiments. Inserts were only included to test its effect on controlling membrane fouling and were only mounted after the gas-lift operation mode was finished. Permeate from the membrane was returned to a plastic pipe that served to adjust the water level in bioreactor. By the use of the plastic pipe, the flux of the membrane could be changed within a wide range. Meanwhile, the inflow and the outflow of the overall reactor was always the same and no dilution of the influent took place. The critical flux was based on a flux step method (Le Clech et al. 2003).

In this experiment, a flux was maintained within 10 minutes followed by a backflush for 6 seconds. After the backflush, the flux was increased by 4 $L/m^2.h$ TMP variation was recorded accordingly.

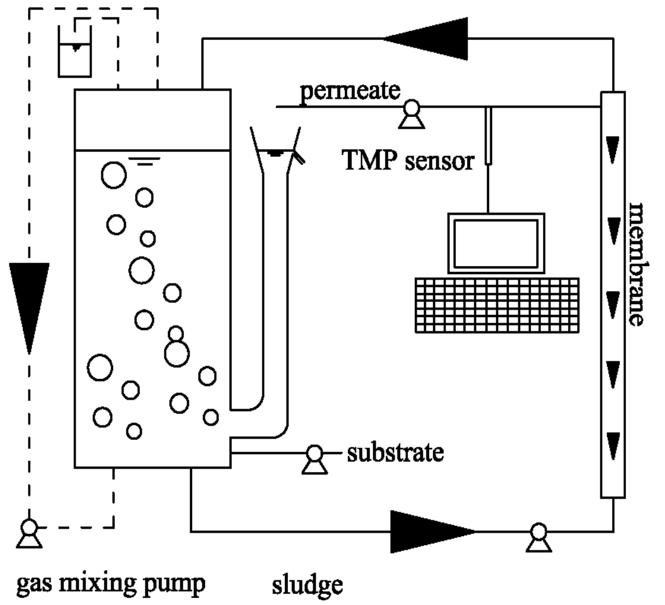

Figure 2.1 Schematic representation of the experimental setup (setup for inserts), the setup for slug flow is shown in figure 1.1 left.

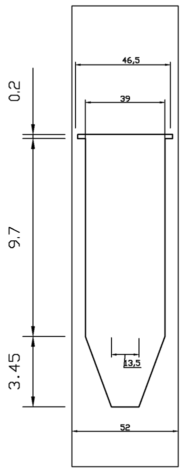

Figure 2.2 The shape and size (mm) of inserts placed in tubular membrane

Inserts were placed in the tubular membrane to test its effect on membrane fouling control. The number of the inserts was up to 20. The distance between each two inserts was 3 cm. They were tied together and kept in place by a plastic wire of 1 mm diameter. Figure 2.2 shows the dimensions of an insert placed in the tubular membrane. Experiments were performed using reactor supernatant for the filtration tests. Compared to anaerobic sludge, the supernatant has similar fouling capacity as indicated by Jeison and van Lier (2007). The supernatant was obtained by overnight settling of the sludge.

Granular sludge was taken from a plant treating wastewater containing lactose (Purac Biochem, Gorinchem, The Netherlands). The sludge was crushed into small particles and inoculated in the bioreactor. The substrate is prepared with gelatin: acetate:

propionate and butyrate to obtain a COD ratio 2:1:1:1. The substrate was diluted with demineralized water until a total COD concentration of 20 g/L. The imposed organic sludge load was 0.3 g COD/gVSS.d. Samples taken from the membrane permeate were injected into the reagent and the temperature was kept at 148 ^oC for 2 hours. Then COD concentration was measured by means of a spectrophotometer (NOVA60). Specific methanogenic activity was measured following pressure increase using the method of Zandvoort (Zandvoort et al. 2002). The linear part of the curve describing methane generation versus time was used to calculate the methanogenic activity. PSD was measured by means of a particle size counter (Model 3000, Pacific Scientific Instruments).

2.3 Results

2.3.1 Effect of Taylor bubble on fouling

Effect of nozzle diameter and gas superficial velocity (U_g) on TMP increasing rate

The influence of gas superficial velocity and nozzle diameter on the TMP increasing rate is shown in Table 2.1. During all the experiments, TMP increased linearly as time passed and TMP increasing rates were calculated accordingly. Data were collected for 1 hour for each experiment except the case where U_g was equal to 0.23 m/s (18 minutes) since the TMP sharply climbed to 400 mbar at this gas velocity. As can be seen in Table 2.1, the decrease in nozzle diameter and the increase in gas superficial velocity resulted in a decrease in TMP increasing rate.

Table 2.1 TMP increasing rate at different gas superficial velocities and nozzle diameters (J=20 L/m^2.h, Dm=5.2 mm)

	TMP increasing rate (mbar/min)		
Nozzle	U_g =0.23 m/s	U_g = 0.48 m/s	U_g = 0.62 m/s
3 mm	20.73	5.21	3.81
5 mm	22.79	5.79	5.11
7 mm	22.79	7.52	6.34

$D_{m:}$ membrane diameter. Standard deviation of each triple measurements was below 5%.

Effect of membrane diameter on membrane fouling

Figure 2.3 shows the TMP development at different membrane diameters and gas superficial velocities. A large membrane diameter provided a high TMP increasing rate, which means that large membrane tube is not suitable to be used in cross-flow membrane bioreactors in terms of membrane fouling.

Therefore, it is clear that 5.2 mm and 3 mm might be the best practical sizes for the membrane diameter and nozzle, respectively. Moreover, a smaller nozzle (1 mm) and membrane tube (3 mm) were also tested. However, the nozzle was easily blocked by particles in sludge with total solid concentration of 40 g/L. The blocking problem was also observed when the smallest membrane (3 mm) tube was used. Thus, it is considered that the nozzle (3 mm) and membrane tube (5.2 mm) are the most suitable sizes for cross flow operation when a high TSS concentration is applied, though the membrane fouling reduction still needs further improvement.

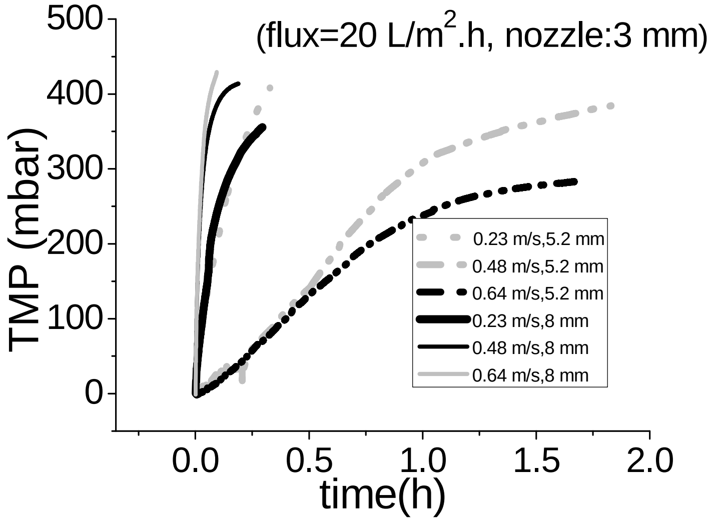

Figure 2.3 TMP increasing rate at different membrane diameters and gas superficial velocities

Effect on permeate quality, particle size distribution and SMA

The influence of shear stress generated by Taylor bubbles on the effluent COD concentration and the COD removal efficiency is shown in Figure 2.4. At the beginning of the experiments, effluent COD concentrations were recorded around 6.4 g/L, likely caused by poor bioreactor mixing. Enhanced mixing immediately resulted in much lower effluent COD values for the next 4-5 weeks. Air intrusion via a broken gas pipe at day 50 resulted in a sharp increase in the effluent COD (Figure 2.4). Full recovery was only observed after 20 days of continuous operation. Results presented in Figure 2.4 indicate that long-term operation is feasible and the sludge activity, in terms of COD removal efficiency, is not negatively influenced by the shear stress generated in membrane module, which is supported by the observed increase in SMA (see the paragraph below).

The impact of shear stress on sludge morphology was investigated by analyzing the PSD during the course of the continuous flow experiment. In addition to the high superficial liquid velocity of 0.34 m/s, the wake zone, which is a secondary flow zone, is generally regarded as high turbulent zone, causing increased shear (Cui et al. 2003). As clearly illustrated in Figure 2.5, the percentage of small particles increased during the experimental run time. Apparently, the anaerobic sludge particles could not resist the shear stress generated by Taylor bubbles in the membrane module. The mean diameter gradually shifted from 20 μm to 5 μm. The decrease in particle size was also discovered in a submerged anaerobic membrane bioreactor in which coarse bubbles were involved (Jeison 2007). SMA experiments conducted at the beginning and at the end of experiment indeed showed an increase from 0.16 g CH4-COD/gVSS.d at day 1 to 0.41 g CH4-COD/gVSS.d at day 70, with a standard deviation of 0.03 g CH4-COD/gVSS.d. The observed increase in SMA might be attributed to the decrease in particle size, reducing substrate mass transfer limitation, and/or the enrichment of the sludge by development of methanogenic microbial subpopulations.

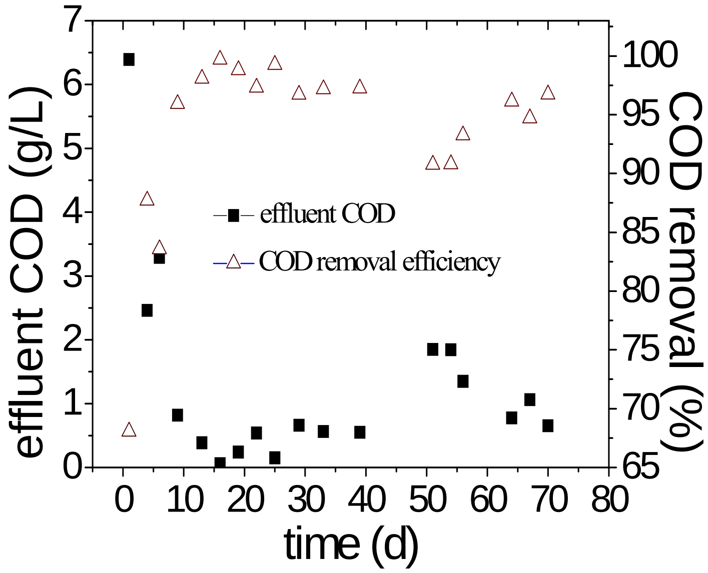

Figure 2.4 COD removal efficiency during operation with Taylor bubbles, U_g=0.74 m/s

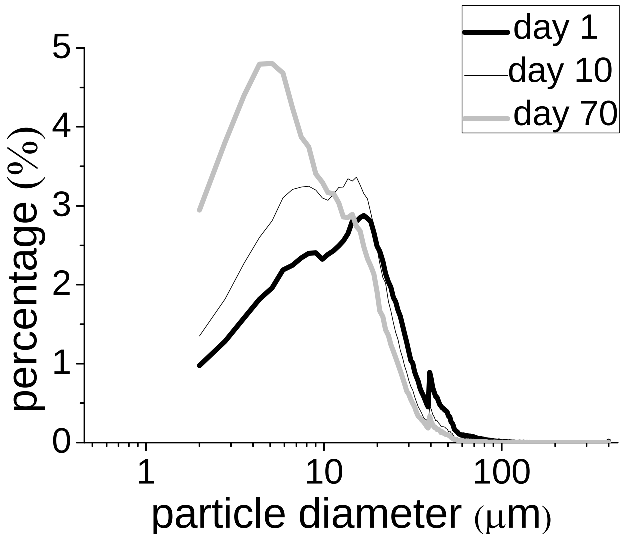

Figure 2.5 PSD in the beginning and end of the experiment (percentage is based on particle number), U_g = 0.74 m/s

2.3.2 Increasing flux by fixed insert

Results in Figure 2.6 clearly show the short-term positive effect of the mounted inserts on supernatant filterability, applying a flux of 34 $L/m^2.h$. In fact, when the inserts were absent, frequent back flush was necessary to lower the TMP. Back flush could be significantly lowered when the inserts were present, whereas the TMP level was lowered by almost one order of magnitude. Very interestingly, Figure 2.6 shows that the use of inserts significantly decreased the TMP increasing rate under the same flow conditions. As can be seen from Figure 2.6b, TMP was maintained at a low level, even while flux was kept high for an extended period of 7 hours. The observed TMP was similar to the data in Figure 2.6 a, which were collected in a short-term experiment.

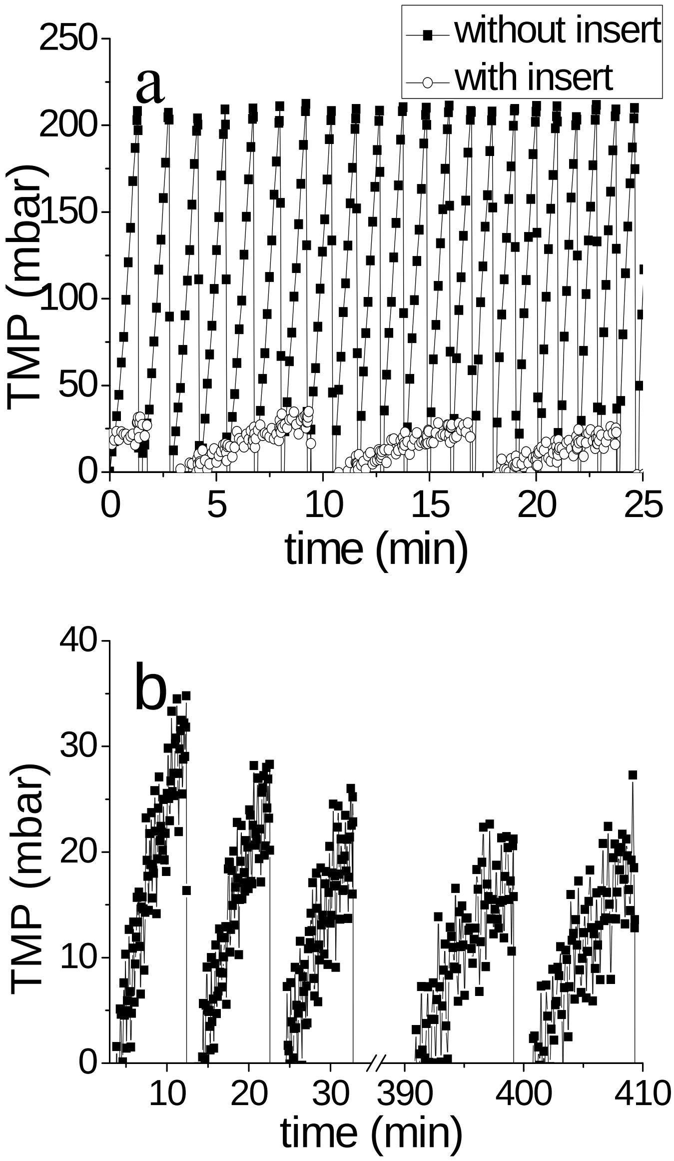

Figure 2.6 a) TMP without and with insert (flux=34 L/m^2.h); b) Extended period of TMP variation with insert (flux=34 L/m^2.h)

The significantly increased stable flux can be explained by the increase in mass transfer at the membrane surface. The mass transfer coefficient at the membrane surface is given by (Taha 2002):

$$k = 1.62\left(\frac{d_m \gamma D}{d_h L}\right)^{0.33} \quad (2\text{-}1)$$

Where k: mass transfer coefficient (m/s); d_m: diameter of tubular membrane (m); d_h: equivalent hydraulic diameter (m); γ: shear rate (l/s); D: mass diffusivity, m^2/s; L: length of tubular membrane (m).

The inserts significantly reduced the equivalent hydraulic diameter of the tubular membrane at the locations where the inserts were mounted in the membrane, which subsequently leads to an increased shear rate in the resulting narrow flow channel, applying the same liquid flow rate. In this way, the use of the inserts increased the mass transfer coefficient at the membrane surface, which resulted in an increased foulant mass transfer from membrane surface to the bulk solution. Therefore, pore blocking and cake layer formation did not easily occur, resulting in the observed increased flux.

2.4 Discussion

A two-phase flow is generally considered effective to alleviate membrane fouling. However, our results clearly indicate the limitations of a two-phase flow for efficient membrane operation at high flux under anaerobic conditions. Apparently additional techniques, such as the application of inert inserts are required to improve the membrane flux. Though the inserts led to a reduction of the membrane fouling in this study, it needs to be stressed that the use of inserts may cause membrane surface erosion that reduces membrane lifespan and requires significant energy input resulting from an increased pressure drop along the membrane, which in our study was 0.5 bar. Additionally, localized clogging at the site of the inserts may reduce the available membrane filtration area. Therefore, the application of inserts should be very carefully evaluated.

Surprisingly, the applied shear stress in the tubular membrane did not decrease the reactor efficiency. It was originally considered that the effect of shear stress on sludge activity comes from two aspects. First, shear stress generated by the biogas bubbles might cause cell lyses. Critical shear stress is defined as the minimal stress applied over a long period causing noticeable damage to the microorganisms (Prokop and Bajpai 1992). For instance, the critical shear stress for *Tetrahymena* lysis is 24 Pa (Midler and Finn 1966). Besides, cells attached to the bubble-liquid interface may suffer significant surface tension forces, which may stretch the cellular lipid bilayer and result in cell damage (Prokop and Bajpai 1992). However, the critical shear and surface tension that cause cell damage to anaerobic microorganisms are not known.

Apparently, shear stress induced cell lyses was not of major importance in the investigated side stream tubular AnMBR and/or was in the same order of magnitude, or less, than the natural decay of methanogenic sludge. According to Siegrist et al. (2002), decay coefficients of anaerobic colonies range between 0.05 d^{-1} and 0.3 d^{-1}, which indicates that the microorganisms that decay with the lowest rate had already varied significantly during the experiment which proceeded over 70 days. Nonetheless, no decrease in reactor performance was observed during the experiment.

The second effect of shear stress on sludge activity comes from the influence on sludge structure. High SMA of granular sludge originates from the fact that colonies of acetogenic bacteria are closely linked with micro-colonies of hydrogenotrophic methanogenic archaea, which allows an efficient interspecies hydrogen transfer (Hulshoff Pol et al. 2004). It was originally considered that high shear stress in the membrane would decrease the PSD and then would lead to a decreased SMA. However, in this study, the sludge characterized by fine particles demonstrated a higher activity compared to original sludge with a larger PSD. It is considered that in large particles substrate diffusion is limited and that the generated fine particles suffer less from substrate diffusion limitation. In addition, biofilms that undergo high shear stress can have a denser structure, which also shortens the distance between the micro-colonies. Both aspects may have played a role in our studies. Similarly, Celmer et al. (2008) also found that a higher shear force applied to a hydrogenotrophic denitrification MBR improved denitrification rates by reducing biofilm thickness.

Finally, the nature of carbon source may also impact sludge flocculation and PSD. It is reported that gelatin, an energy-rich substrate that was also used in our present work, may play a role in preventing activity loss. EPS, which is excreted by microorganism, plays a key role to connect microorganisms to form activated sludge (Liao et al. 2001, Wilen et al. 2003) and offers stability in high shear environments (Mikkelsen et al. 2002). Energy-intensive substrates result in higher amounts of EPS, compared to less energy intensive substrates.

2.5 Conclusions

The Taylor bubble approach did not offer a satisfactory effect on fouling control while the membrane module was operated in a gas lift mode under anaerobic condition. Therefore, in addition to the use of the bubbles, additional techniques are required to improve membrane fouling control.

The application of inert inserts could significantly improve achievable flux to levels as high as 34 $L/m^2.h$.

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Chapter 3

Analysis of mass transfer characteristics in a tubular membrane using CFD modeling

Chapter 3 Analysis of mass transfer characteristics in a tubular membrane using CFD modeling

Abstract

In chapter 2, it was found that TMP increased very fast despite using various gas superficial velocities in the applied tubular membrane. It is proposed that either a weak foulant mass transfer capacity from membrane surface to sludge bulk solution or a very bad sludge filterability was responsible for the quick TMP increase. In contrast to the large amount of research into aerobic membrane bioreactors, little work has been reported on anaerobic membrane bioreactors (AnMBRs) in which membrane fouling resulting from cake layer formation is a key issue. Membrane fouling generally occurs more seriously in AnMBRs than in aerobic membrane bioreactors. However, membrane fouling could be managed through the application of suitable shear stress that can be introduced by the application of a two-phase flow. When the two-phase flow is applied in AnMBRs, little is known about the mass transfer characteristics, which is of particular importance, in tubular membranes of AnMBRs. In this chapter, fluid dynamic modeling was employed to analyze the mass transfer characteristics in the tubular membrane of a side stream AnMBR in which, gas-lift two-phase flow was applied. The modeling indicated that the mass transfer capacity at the membrane surface at the noses of gas bubbles was higher than the mass transfer capacity at the tails of the bubbles, which is in contrast to the results when water instead of sludge is applied. At the given mass transfer rate, the filterability of the sludge was found to have a strong influence on the TMP at a steady flux. In addition, the model also showed that the shear stress in the internal space of the tubular membrane was mainly around 20 Pa but could be as high as about 40 Pa due to gas bubble movements. Despite the presence of these high shear stresses, a stable PSD was found for sludge particles.

3.1 Introduction

High concentrations of active biomass are required for successful anaerobic biological wastewater treatment. The biomass concentrations in bioreactors can be increased through the granulation of anaerobic biomass that allows the decoupling of hydraulic retention time from biomass retention time. However, with specific wastewaters such as those with high particle contents and high salinity levels, the granulation of anaerobic sludge particles is not always successful. Alternatively, high sludge concentration can be realized by combining membranes and anaerobic bioreactors. The introduction of membranes is, however, accompanied by the problem of membrane fouling, which means that either a membrane flux declines, while a constant TMP is maintained, or TMP increases while a constant flux is maintained. Membrane fouling therefore needs to be strictly controlled if anaerobic membrane bioreactors (AnMBRs) are to become more widely applied.

Many strategies for controlling membrane fouling have been tested (Meng et al. 2009, Wakeman and Williams 2002), of which the application of a gas-lift two-phase flow (slug flow) is regarded as effective (Cui et al. 2003). Slug flow increases the shear stress on the membrane surface, which in turn promotes mass transfer from membrane surface to a bulk solution and eventually allows membrane fouling to be controlled to a certain extent (Jeison and van Lier 2006). In slug flow, the liquid in front of a gas slug is replaced by the gas slug and then mixed by the liquid at the tail of the gas slug. The mixing generates a turbulent wake zone (Cui et al. 2003, Lindeboom et al. 2011), which is believed to promote the mass transfer from membrane surface to a bulk solution. In order to characterize the two-phase flow in MBRs, an electro-chemical method has been used in an aerobic MBR in which many bubbles were generated through the application of aeration nozzles (Zhang et al. 2009), but the response of biomass to this electro-chemical method has yet to be reported.

Computational fluid dynamics (CFD) is able to characterize flow conditions in various situations and has been widely applied as a powerful tool for studying flow dynamics. For instance, extensive investigations were carried out to know gas-liquid flow conditions in tubular membranes using CFD modeling (Cui et al. 2003). Their modeling revealed that the shear stress at a membrane surface gradually increases along a film zone, i.e. a thin zone between a gas bubble and a tubular membrane surface, and rapidly decreases in the wake zone behind the bubble. In addition, Ratkovich et al. (2009, 2011) showed by CFD-modeling that the hydrodynamics of two-phase flow in tubular membranes is similar to that reported by Cui et al. (2003). In Cui's and Ratkovich's modeling studies, a low concentration of dextran and aerobic sludge was used to simulate the behavior of the mixtures, respectively. However, the hydrodynamics of particulate concentrated sludge is probably different from that of the diluted sludge and dextran mixtures since particulate concentrated sludge is a non-Newtonian liquid and the relationship between shear stress and shear rate is non-linear. It is, therefore, not likely that these previously published CFD modeling results are applicable to similar situations in which sludge with a TSS concentration as high as 40 g/L is involved.

CFD modeling can be applied to assess mass transfer characteristics in tubular membranes in which slug flow is applied. It has been reported that gas slugs have limited capacity to control membrane fouling in a sidestream AnMBR (Jeison et al. 2009, Yang et al. 2011), and that the TMP increased rapidly even when a flux as low as about 10 L/m^2.h was applied (Jeison and van Lier 2007). The results might be related to the characteristics of the used sludge. Sludge is a non-Newtonian liquid, which may influence mass transfer characteristics in a tubular membrane and thereby restrict achievable fluxes. It is, therefore, important to understand the hydrodynamic conditions within a tubular membrane. Hence, CFD modeling was used to characterize the hydrodynamics of sludge within a tubular membrane. The model quantified shear stresses in the bulk solution and at the membrane surface, as well as the mass transfer capacity between the liquid and sludge particles.

3.2 Materials and methods

The experimental set-up is shown in Figure 1.1 (left) and the AnMBR operation is explained in Chapter 2. Figure 3.1 shows the dimensions of the membrane module. The bottom of the channel was connected to a Y connector and the two portals of the Y connector were used as inlets for gas and biomass, respectively. The superficial velocity in the tubular membrane was 0.34 m/s for liquid and 0.74 m/s for gas. The liquid velocity was induced by gas motion since no pump was used for the sludge. Other liquid velocities could be realized simply by changing the gas velocity (Chapter 1). The theory proposed by (Dziubinski et al. 2004) infers that these superficial velocities for sludge and biogas produce slug flow in the tubular membrane. The liquid and gas velocities are optimized velocities. Decreasing the velocities will decrease the slug flow's capacity of removing foulants from the membrane surface to bulk solution. Increasing the velocities to too high levels might change the slug flow into a churn flow, which also will decrease the capacity of the two-phase flow for fouling control (Chapter 1).

The particle size was measured using an HIAC ChemShield (Pacific Scientific Instruments), which uses laser light-scattering as a sensing method for particle sizes within the 0.1 µm to 0.4 µm and 0.5 µm to 5 µm size ranges. For the particle size measurements, sludge samples were taken out of the reactor and were first diluted with water by a factor of 80 and then analyzed. The decrease in ion strength may deflocculate sludge particles (Wilen et al. 2004). Therefore, in order to prevent the deflocculation of sludge particles, the ionic strength of the dilution water was equal to that of the sludge. During the sludge filterability test, a pump maintained the flux across the membrane. Two types of sludge were used in the filterability test: an active flocculant anaerobic sludge (Sludge A) that was inoculated in the reactor and the sludge that was stored for one month at room temperature after feeding had been stopped (Sludge B).

CFD model

We modeled the flow within the y-shaped inlet channel. The model used a two dimensional computational domain that was created for the CFD model, and the domain (shown in Figure 3.1) was used by commercially available FLUENT software (version 6.3.26). The model used a 2D space structure other than axisymmetric structure, because the 2D space structure allowed two inlets to be included in the model, which matched the real conditions, although at the cost of computational power. There were 44,184 cells, whose volumes ranged from 1.06×10^{-9} m^3 to 2.9×10^{-7} m^3. Fine grids were used at the membrane wall surface and the model results were independent of the applied grid sizes.

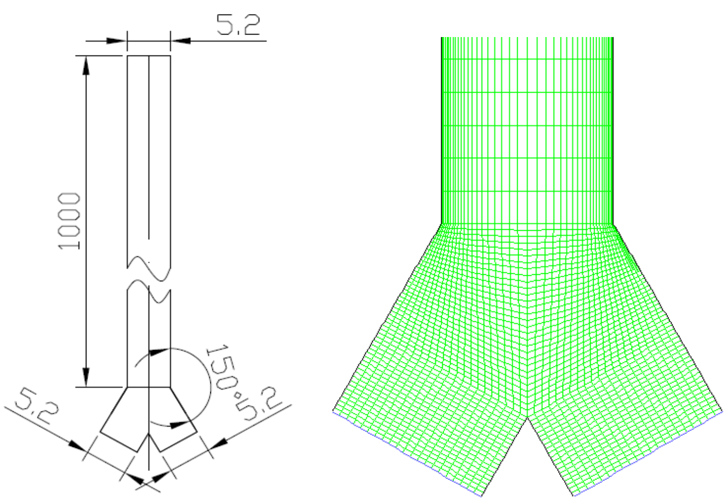


Figure 3.1 Left: Dimensions of the membrane module (mm): modeling domain in CFD Right: grids of the inlets in the model

The method of solution used a pressure-based 2D unsteady solver, with explicit two-phase Volume Of Fluid modeling for handling the multiphase of sludge and biogas. Because there was no pure laminar flow in the tubular membrane, a turbulent model and a laminar model were applied. However, the laminar model did not converge. Therefore, RNG k-epsilon turbulent model was chosen for turbulence modeling and an enhanced wall treatment approach was used. PISO method was used for pressure-velocity coupling. PRESTO!, Second Order Upwind, and Geo-Reconstruct methods were selected for pressure, momentum, and volume fraction, respectively. In addition, the Second Order Upwind method was used for turbulent dissipation rate discretization. The two portals at the bottom of the modeling domain shown in Figure 3.1 were set as liquid and gas inlets. Simulations were carried out for two sets of superficial gas and liquid velocities, which provided two different models. In the two models, only superficial gas and liquid velocities were different. In one model, the superficial velocities in the membrane module were 0.74 m/s for gas and 0.34 m/s for liquid, while in the other model they were 0.48 m/s for gas and 0.32 m/s for liquid.

Viscosity determination in the model

The rheometry of biomass deviated significantly from plain water or a liquid with a low particle concentration. The relationship between shear rate and viscosity was determined by a universal dynamic spectrometer (Paar Physica UDS 200). The measured rheology of the used anaerobic sludge can be seen in Chapter 4. Eleven shear rates were selected during the viscosity measurement and more viscosity measurements in which more shear rates were applied did not show deviation. Therefore, the measured viscosities can be considered representative.

The viscosities of the liquid at all shear rates were incorporated into FLUENT. FLUENT provides four viscosity models, i.e. Power Law model, Carreau Model, Cross Model and Herschel-Bulkley model, for providing viscosities of non-Newtonian liquids (Fluent.Inc 2006). The model parameters vary according to real viscosities of a liquid. Because these viscosity models could not fit the measured sludge viscosity well, none of the non-Newtonian models offered by FLUENT could be applied for adding viscosity to the model. However, unmeasured viscosities still could be determined by a linear interpolation method.

The interpolation method for viscosity determination was programmed, which was written in C language, and was thereafter incorporated into FLUENT by the use of User Defined Function that is provided by FLUENT for expanding its ability. By the use of the program through User Defined Function, shear rate at each point in the flow field modeled was obtained first by the program and then used for determining the viscosity at that point.

Model validation

Model validation requires detailed insight of pressure difference in the membrane during passage of a gas slug bubble. Pressure variations during bubble passage either can be measured using real time pressure measurement or mathematically modeled.
Pressure measurements were done by placing a pressure sensor at the outlet of the tubular membrane to record pressure fluctuations. However, the real time pressure measurement of a bubble appeared to be impossible due to the limited recording

speed. In fact, the minimum interval of recording of the used pressure sensor was one (1) second, which was too long to capture the real time pressure fluctuation caused by each bubble.

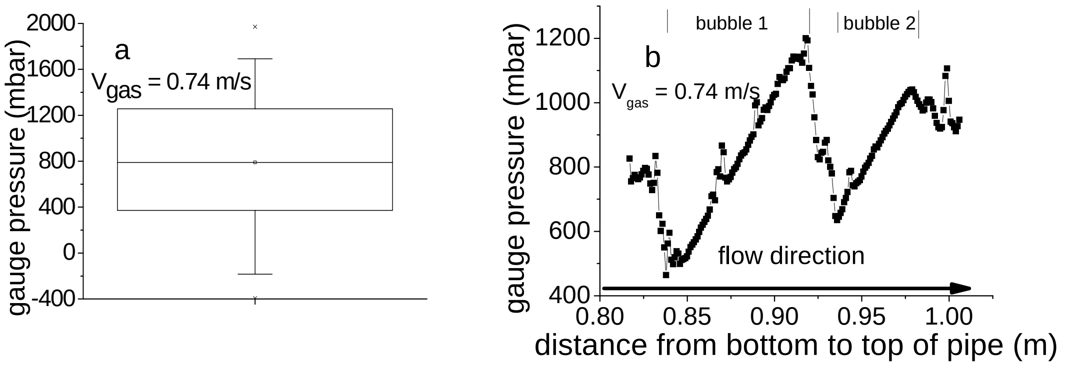


Figure 3.2 Model verification: a) Statistical box chart of measured pressure fluctuations at the outlet. b) Modeled pressure fluctuations in top part of module, close to the outlet

For further calculations and modeling, an imaginary bubble was statistically constructed in the inside-out membrane giving the pressure variation between 400 and 1200 mbar (Bubble 1 in Figure 3.2b). Figure 3.2a includes gauge pressures that were obtained during a measurement that lasted 4 minutes, but the exact number of bubbles that passed the outlet of the tubular membrane was not recorded. Shaping Bubble 1 was done by measuring one point of each bubble passing the membrane tube, each time at another point along the bubble. The pressure varied from 0 to 1600 mbar at most. However, most of the pressure variations were between 400 to 1200 mbar. We realize the limitations of our current approach in model validation. However, more in-depth measurements, such as reported by (Lindeboom et al. 2011) and (Ratkovich et al. 2009), were not available in the present experimental set-up.

3.3 Results and discussion

The turbulence and shear resulting from a bubble's motion produced three effects in the tubular membrane: (1) it enhanced the mass transfer between membrane surface and bulk solution, (2) it broke sludge particles into smaller particles, and (3) it enhanced the substrate mass transfer in the sludge.

Mass transfer at membrane surface

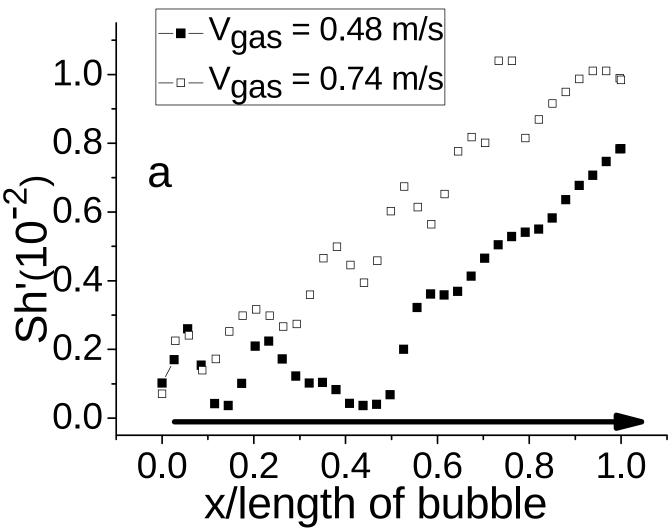
Generally, at the same liquid velocity, slug flow enhances the mass transfer between membrane surface and bulk solution, compared with the mass transfer capacity achieved by only a liquid flow. The mass transfer capacity appears to largely determine the membrane-fouling rate: a high mass transfer capacity, which is represented by a high Sherwood number, results in a good control of membrane fouling. The Sherwood number is described by Equation (3-1) that describes mass transfer between wall surface and turbulent liquid (Beek et al. 1999).

$$Sh = 0.027 \times \mathrm{Re}^{0.8} Sc^{0.33} = 0.027 \times \frac{(Vd_{pi})^{0.8}}{\eta^{0.47}} \times D^{-0.33} \quad (3\text{-}1)$$

$$Sh' = 0.027 \times \frac{(V' d_{pi})^{0.8}}{\eta^{0.47}} \quad (3\text{-}2)$$

Where Sh = Sherwood number, V = mean fluid velocity in the flow channel (m/s), d_{pi} = pipe diameter (m), η = kinematic viscosity (m^2/s), D = diffusion coefficient (m^2/s), Sh' = local Sherwood number, and V' = local velocity of bulk liquid near the membrane surface (m/s).

The transfer of material from membrane surface to bulk solution should only be influenced by the motion of liquid that is in the area immediately surrounding the material of interest. In our case, Equation (3-1) may just be used to roughly estimate a mass transfer capacity of the overall membrane at most, but it is unlikely to be able to provide an exact Sherwood number distribution at the membrane surface around a gas slug because slugs always disturb the flow. However, by replacing the mean liquid velocity with the local velocity close to the membrane surface, it is possible to obtain a local Sherwood number (Sh') distribution around a gas slug. In addition, Equation (3-1) indicates that the local Sherwood number (Sh') concerns the region close to the membrane in which high mass transfer is likely to occur, because a low local liquid velocity correlates with a low mean liquid velocity and a high local liquid velocity correlates with a high mean liquid velocity. The local Sherwood number is universal to any materials with different diffusion coefficients; therefore, D is omitted in Equation (3-2).



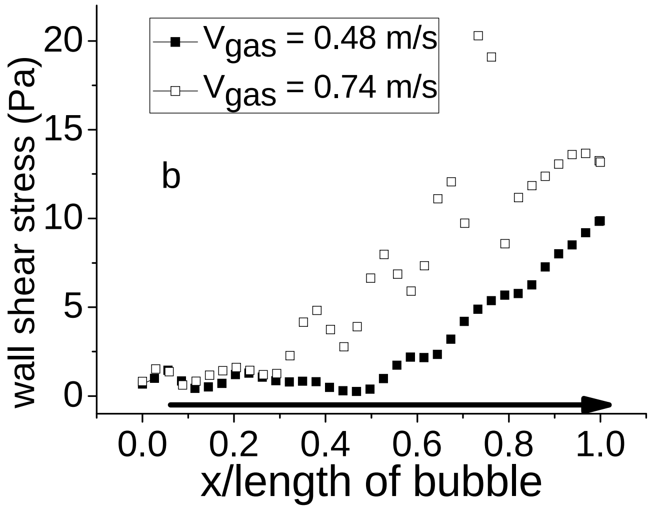


Figure 3.3 Local Sherwood numbers (a) and shear stress distributions (b) at the membrane surface around bubbles at different gas velocities. The arrows show the movement direction of the bubbles

The local Sherwood number around a typical gas slug at the membrane surface is shown in Figure 3.3a. For a bubble moving upwards in a liquid, the circular or oval part of the bubble is defined as the nose of the bubble, whereas the counterpart of the bubble is defined as the tail of the bubble. The local Sherwood number decreases from the nose of a bubble to the tail of the bubble. In contrast to a previous report (Cui et al. 2003), it appears not to be the wake zone at the tail of a bubble that provides the highest mass transfer capacity at membrane surface, but the head zone at the nose of the bubble. This conclusion is also supported by the shear stress distribution shown in Figure 3.3b, since a high shear stress leads to a high mass transfer capacity. It must be noted that the conclusion would be more convincing if a stronger validation of the model can be performed. However, our results are in agreement with previously published work in which particle movement was measured using a high-speed camera along various types of gas slugs (Lindeboom et al. 2011). In that work, highest particle velocity occurred at the nose of the gas slugs with a particle flow direction towards the slug nose. Although wake turbulence seemed to increase with decreasing slug size its contribution in particle movement was less than the nose region.

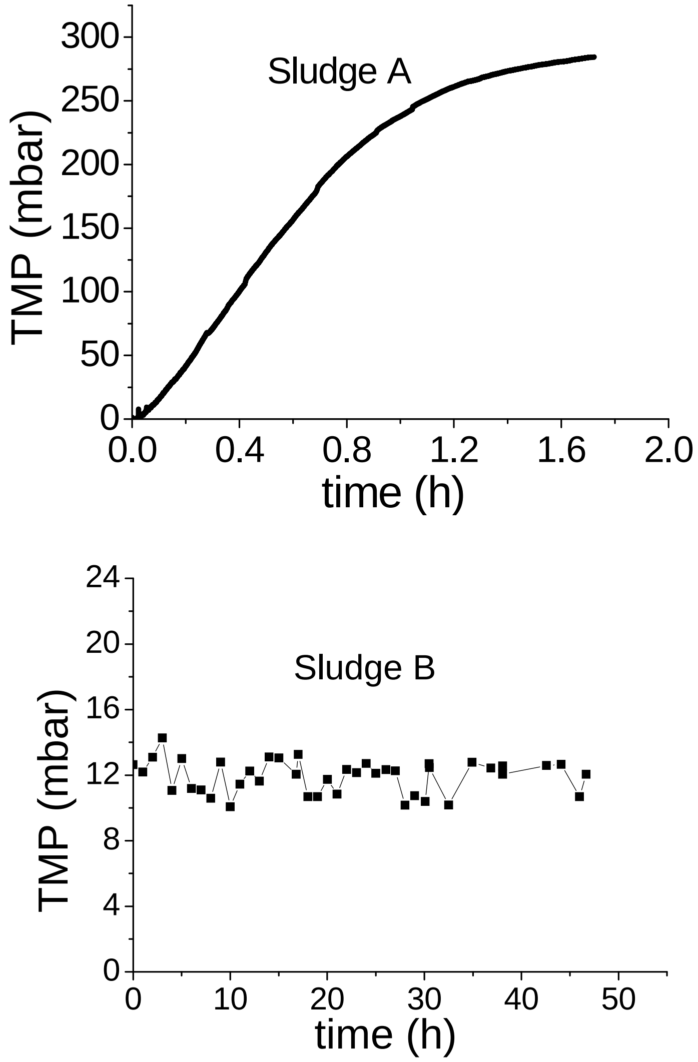


Figure 3.4 TMP variation versus time for sludge A and B (flux = 25 L/m^2.h), V_{gas} = 0.74 m/s

Unfortunately, the resulting mass transfer rate shown in Figure 3.3 could not ensure a sustainable high flux because the hydraulic condition is only one of the factors that influence membrane fouling. As shown in Figure 3.4, the TMP increased at quite different rates when different types of sludge were used as bulk solutions, while other conditions such as the gas velocities remained the same. The filterability of two kinds of sludge was tested at the resulting mass transfer rate shown in Figure 3.3. Sludge A was a normal anaerobic sludge, and Sludge B was derived from Sludge A by stopping the feed to the reactor for a period of one month. Using Sludge B, the TMP did not increase when a high flux was applied. However, using Sludge A, under the same applied cross flow conditions, the TMP increased rapidly at the same flux. It is not clear what exactly happened to the Sludge A that transformed into Sludge B that had much better filterability. However, it turned out that a sustainable high flux could therefore be achieved under the applied slug flow conditions, but it depended on the characteristics of the filtered sludge.

Effect on particle size

Another effect of turbulence (shear stress) induced by bubble motion is breaking up sludge particles into smaller particles (Jeison et al. 2009, Chapter 2). This is not a desirable effect since the decrease in particle size may result in very poor sludge filterability. Moreover, a very high shear stress leading to full dispersion of the biomass particles might negatively impact syntrophic interactions in the sludge, potentially leading to a reduced anaerobic conversion capacity. Therefore, shear stress on anaerobic particles should be well managed, in order to maintain the required juxtaposition of acetogenic and methanogenic species (Stams and Plugge 2009). However, long-term experiments showed that acetogenic sludge activity is preserved in side stream AnMBRs applying cross flow velocities of 1.5-2.0 m/s and gas velocities of 0.1 m/s (Jeison and van Lier 2007). Other authors reported negative influences on bioreactor performance due to strong mixing (Kim et al. 2002, McMahon et al. 2001), but the authors did not provide an exact description of the hydrodynamic conditions within their bioreactors and hence the relationship between shear stress and biomass activity remains unclear.

When a high shear stress is applied in a tubular membrane, a decrease in particle size should be minimized in order to preserve both sludge filterability and the acetogenic sludge activity, as indicated by Kim et al. (2001) and Padmasiri et al. (2007). Many factors can influence the diameters of sludge particles: high biomass age (Knocke and Zentkovich 1986), ionic strengths (Zita and Hermansson 1994), and dissolved oxygen concentrations in aerobic bioreactors (Li and Ganczarczyk 1993) lead to larger particle sizes, as do lower temperatures (Govoreanu 2004). The maximum stable particle diameter can be described by:

$$d_{\max} = \frac{C}{G^n} \tag{3-3}$$

$$G = \sqrt{\frac{\varepsilon_a}{\eta}} \tag{3-4}$$

Where C is the floc strength constant, n is the stable floc size exponent, G is the average velocity gradient, ε_a is the average energy dissipation rate, and η is the kinematic viscosity (Kusters 1991).

Theoretical calculation of the stable particle diameter for a sidestream AnMBR based on Equations (3-3) and (3-4) is, unfortunately, problematic due to reasons such as the kinematic viscosity of sludge is location specific due to the biomass liquid's non-Newtonian behavior.

In order to obtain a correlation between hydrodynamic condition and sludge particle size, the shear stress distribution was derived from the CFD model and particle size variations were measured for the shear stress conditions. The shear stress distribution around a single gas slug is shown in Figure 3.5. High shear stress occurs mainly at the nose and tail of the bubble. However, as shown in Figure 3.5, the shear stress of the bulk solution in the wake of the bubble did not affect the membrane surface as strongly as it did in the nose of the bubble. This explains the lower shear stress at the membrane surface around the tail of the bubble and the higher shear stress around the nose of it. Our present modeling results are in agreement with the observations done by Lindeboom et al. (2011) regarding particle velocity along the bubble. The highest shear stress in the bulk solution was up to 40 Pa, but it is hard to find similarly high shear stress anywhere in the film zone between the bubble and the membrane surface. Interestingly, particle velocity as measured by Lindeboom et al. (2011), approached zero (0) between the bubble and solid surface, coinciding with the calculated low shear stress in that area.

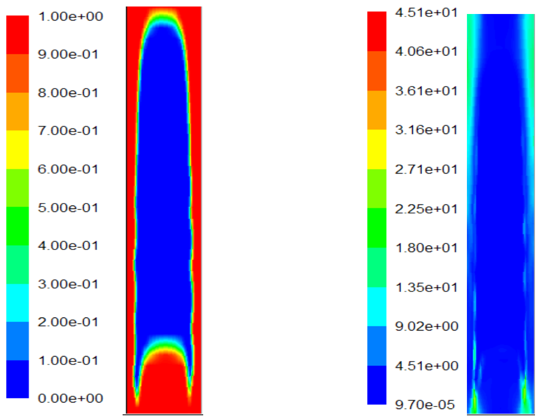


Figure 3.5 Shear stress around a gas slug.
Left: shape of a slug bubble; right: shear stress distribution over the region shown on the left (red: high shear stress; blue: low shear stress, Pa); V_{gas} = 0.74 m/s

In the reactors, a stable PSD exists (Figure 3.6a) for the given shear stress distribution shown in Figure 3.5. The gas superficial velocity did not alter the distribution of particle size of anaerobic biomass within 30 days, which indicates that the PSD depicted in Figure 3.6 was stable under the applied operating conditions. A not altered PSD was also observed at a different gas velocity (Figure 3.6b). Therefore, the PSD is considered stable at a given shear stress, which is in contrast to a previously reported finding (Chapter 2), possibly because sludge may require a certain period of time in which to adapt to the shear stress, or to the reactor conditions. Variation in the PSD of sludge in the bioreactor was observed over a 70-day period (Chapter 2) but the PSD subsequently reached a stable state for that particular shear stress.

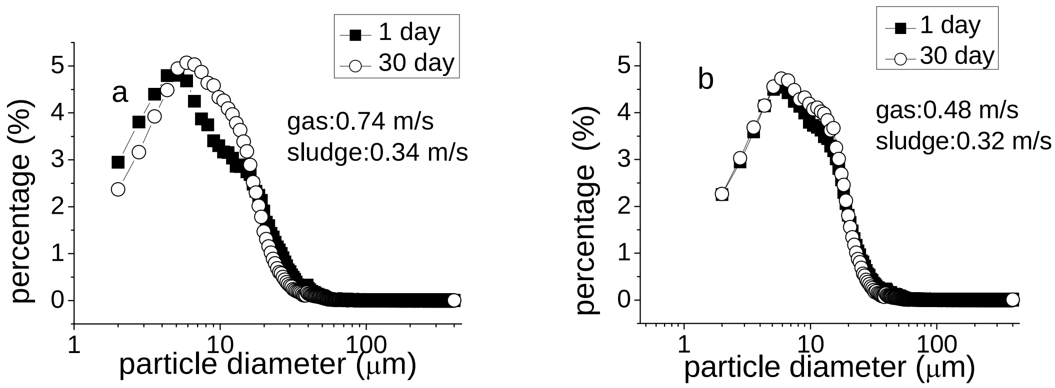


Figure 3.6 Particle size distributions for different superficial velocities: a) gas 0.74 m/s, sludge 0.34 m/s and b) gas 0.48 m/s, sludge 0.32 m/s

The enhanced substrate mass transfer in sludge

Yet, another effect is the promotion of mass transfer, not only between the membrane surface and the bulk solution, which can alleviate membrane fouling, as has been demonstrated by previous researchers (Cui et al. 2003), but also between the bulk solution and sludge particles. The latter mass transfer can be quantified by Equations (3-5) to (3-8) (Hooijmans et al. 1990):

$$J_s = K_I(C_{sI} - C_{si}) \tag{3-5}$$

in which

$$K_I = D/\delta_s \tag{3-6}$$

where

$$\delta_s = d_p / Sh \tag{3-7}$$

and

$$Sh = 2 + \frac{0.66}{[1+(0.84Sc^{\frac{1}{6}})^3]^{\frac{1}{3}}} \times \frac{(\mathrm{Re}\times Sc)^{1.7}}{1+(\mathrm{Re}\times Sc)^{1.2}} \tag{3-8}$$

Where J_s is the surface substrate flux (g/m^2.s), K_I is the mass transfer coefficient (m/s), C_{sI} is the substrate concentration in the liquid (g/m^3), C_{si} is the substrate concentration at the interface (g/m^3), δ_s is the thickness of the liquid boundary layer (m), d_p is the particle diameter (m), Sh is the Sherwood number, Re is the Reynolds number (=v×d$_p$/ η) in which v is the liquid velocity (m/s) and η is the kinematic viscosity (m^2/s), Sc is the Schmidt number (η/D) in which D is the diffusion coefficient (m^2/s), The diffusion coefficient of acetic acid is equal to 1.29×10^{-9} m^2/s.

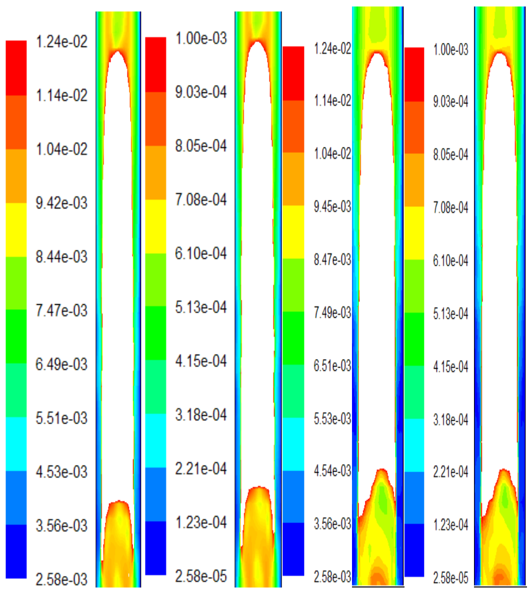


Figure 3.7 Mass transfer coefficient (K_l) around a gas slug for different gas velocities and particle sizes ((red: high K_l; blue: low K_l). From left to right: V_{gas}=0.74 m/s (first: d_p =1 μm; second: d_p =100 μm) and V_{gas} = 0.5 m/s (third: d_p =1 μm; fourth: d_p =100 μm)

By increasing the turbulence, the Sherwood number in Equation (3-8) is also increased, which eventually leads to an increase in the mass transfer coefficient (K_I) and the surface substrate flux (J_s). The mass transfer coefficient distributions are given in Figure 3.7. The zones at the tail and nose of a gas slug are zones in which mass transfer is enhanced. The film zone, which is the zone between the gas slug and the membrane surface, has a lower mass transfer coefficient. Moreover, Figure 3.7 indicates that smaller particle diameters lead to higher mass transfer coefficients at the surface of the particles, which favors biochemical reactions. Nonetheless, compared to the overall conversion capacity in the reactor bulk, the contribution of the anaerobic conversion capacity in the tubular membranes is very limited, even if this capacity is enhanced.

3.4 Conclusions

The mass transfer characteristics in a tubular membrane operated under anaerobic and slug-flow conditions have been analyzed using a CFD model. The CFD model revealed that the mass transfer rate between membrane and bulk solution decreased from the nose of the bubble to the tail of the bubble, which is in contrast to the results when water was used instead of sludge. At the applied shear stress of about 20 Pa at the membrane surface, a membrane flux of 25 $L/m^2.h$ was achieved in the side stream AnMBR. Nonetheless, the achievable flux depended largely on the filterability of the sludge under the attained mass transfer conditions provided by the bubbles in the tubular membrane.

The shear stress in the internal space of the tubular membrane was on average about 20 Pa but could reach up to 40 Pa. However, the increased shear did not affect particle size distribution. The CFD model also showed that the zones at the nose and the tail of a bubble promoted mass transfer between the bulk solution and sludge particles.

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Chapter 4

Non-feasibility of adsorbents for fouling control in anaerobic membrane bioreactors

Chapter 4 Non-feasibility of adsorbents for fouling control in anaerobic membrane bioreactors

Abstract

Chapter 3 indicates that the applied slug flow enabled operating a tubular membrane with a membrane flux over 20 L/m^2.h in a short-term experiment, which was attributed to the filterability of sludge. Therefore, under the applied operation condition that determines mass transfer in a tubular membrane, focus should be on improving sludge filterability in order to control the membrane fouling. The research presented in this chapter deals with the application of adsorbent to increase the filterability of anaerobic sludge. Addition of PAC enhanced the effect of slug flow on membrane fouling control. However, the combined effect was still considered not being significant. Considering the fact that the PAC had limited capacity in fouling control, and the removal it would lead to biomass loss, a new kind of adsorbent should be applied, which aimed at avoiding biomass as much as possible during adsorbent removal. Therefore, a magnetic adsorbent with an approximate particle diameter of 1 μm was manufactured and used for fouling control in an anaerobic membrane bioreactor, equipped with a side flow inside-out tubular ultra-filtration membrane, operated under slug flow conditions. Short-term experiments prior to adsorbent dosing, showed that the applied slug flow conditions enabled membrane operation at a flux exceeding 20 L/m^2.h, with a low TMP increasing rate. Then, the magnetic adsorbent (1 g/L) and subsequently more magnetic adsorbent was added in order to increase the concentration of the adsorbent from 1 g/L in the reactor to 5 g/L. However, the introduction of the magnetic adsorbent resulted in an increased TMP, even at the low concentration applied (1 g/L). The TMP increasing rate increased with the applied adsorbent concentration. Strikingly, addition of the adsorbent had no effect on sludge viscosity, although filterability deteriorated significantly. Removal of adsorbent from the sludge using an external magnetic field was unfortunately accompanied by significant biomass loss. Hence, under the applied conditions, the proposed methodology is not considered viable for fouling or membrane flux control.

4.1 Introduction

Since the introduction of membranes into wastewater treatment, the problem of membrane fouling has attracted considerable attention. It was found that anaerobic sludge has worse filterability than aerobic sludge while components in the supernatant of anaerobic sludge play the most important role in membrane fouling (Spagni et al. 2010). Similarly, it was stated that fine colloids in original anaerobic broth is responsible for the resistance of a cake layer, though its amount is small (Choo and Lee 1996a, b, Kang et al. 2002), which explains a good filterability of mesophilic sludge over a thermophilic sludge that contains a larger fraction of colloids (Lin et al. 2009).

Many methods for controlling membrane fouling have been proposed by researchers. Among these methods, adsorbent dosing has been widely tested. The adsorbents include carbon black, PAC and zeolite (Lohwacharin et al. 2010, Remy et al. , Wu et al. 2009). Since PAC can absorb organic contaminants that may be responsible to membrane fouling and then lead to higher possible flux (Akram and Stuckey 2008, Hu and Stuckey 2007, Park et al. 1999, Vyrides and Stuckey 2009), PAC was also added into the AnMBR to enhance the effect of Taylor bubble. The enhancement was based on the assumption that the Taylor bubble enhances mass transfer from the membrane surface to the sludge, while PAC reduces the concentration of colloidal contaminants that are less susceptible to shear-induced diffusion. It is obvious that possible enhancement depends on the dose of PAC. However, a large PAC dose does not lead to a better effect. Unfortunately, no consensus exists on the optimal dose. It was reported that the addition of PAC at the dose of 3.4 g/L made the membrane less permeable (Akram and Stuckey 2008). However, other research did not found the worsen effect, while even a higher dose (5 g/L) was tried (Park et al. 1999). The addition of a low dosage of PAC results in a significant reduction in membrane fouling or increased membrane flux, through enhanced scouring of the membrane surface by PAC particles, through adsorption of membrane foulants by the PAC and their subsequent biodegradation, and through the positive effect that PAC has on the strength of sludge flocs (Remy et al. 2009). However, overdosing with PAC or zeolite may fail to reduce membrane fouling because of their potential to become foulants themselves, either through the formation of a cake layer or by blocking membrane pores (Wu et al. 2009).

In addition to the limited ability of PAC to control membrane fouling under anaerobic conditions, also the regular replacement of used and no longer active PAC from bioreactors forms a constraint for application (Ng et al. 2006). Moreover, the removal of PAC from AnMBRs inevitably results in biomass loss, thereby reducing the sludge concentration and thus reducing the volumetric loading capacity. Particularly for anaerobic reactors, unnecessary sludge loss should be prevented because anaerobic sludge grows slowly, which is a constraint of dosing PAC into AnMBR. Application of adsorbents that selectively can be removed, without affecting the biomass concentration, would represent an interesting alternative, tackling this constraint.

Adsorbents generally can be classified into four categories based on whether it is effective in controlling membrane fouling and whether the removal of it will cause sludge loss.

The preferred adsorbent for AnMBR systems is both effective in membrane fouling control and does not cause sludge loss. Magnetic adsorbents have been used in mineral processing, wastewater treatment, molecular biology, cell sorting, and clinical diagnostics (Franzreb et al. 2006, Liao and Chen 2002a). The very high surface area to volume ratio of the magnetic adsorbent, together with its non-porous nature, results in a high binding capacity and very rapid adsorption kinetics. It has been postulated that colloids are important foulants (Rosenberger et al. 2006) and that pure magnetic iron oxide can significantly reduce the concentration of dissolved and colloidal organic substances in wastewater (Franzreb et al. 2006). In principle, magnetic adsorbents can be selectively removed from the reactor broth using an external magnetic field. Therefore, magnetic adsorbents are of interest to control membrane fouling, provided selective removal is not accompanied with significant sludge loss. Currently, the full nature and potential of magnetic adsorbents is not known giving incentives to further research the use of magnetic adsorbents to combat membrane fouling in AnMBR.

4.2 Materials and methods

AnMBR operation

A schematic view of the setup is depicted in Chapter 1, Figure 1.1 (left). The operation of the AnMBR is further described in chapter 2 as well as the method for particle size distribution measurement in the range 2 - 400 µm. A universal dynamic spectrometer (Paar Physica UDS 200) was used to characterize the rheology of the sludge. The amount of total suspended solids and volatile suspended solids was measured following APHA Standard Methods (Eaton et al. 2005). Two types of sludge were used in the filterability test: Sludge A and Sludge B. The source of Sludge A and Sludge B is described in Chapter 3.

Adsorbent

The magnetic adsorbent was prepared following the procedure described by Liao and Chen (2002b), by adding 0.1 mol/L $FeSO_4.7H_2O$ to 0.2 mol/L $FeCl_3.6H_2O$ in demineralized water. The pH of the solution was then rapidly increased by adding ammonia solution (25%) and maintained at a pH of 10. During this operation, the solution was stirred vigorously with a magnetic bar. The magnetic adsorbent was then allowed to precipitate. After decanting the supernatant, the adsorbent was rinsed several times using demineralized water and ethanol alternately. The adsorbent was then placed in an oven for 30 minutes at 80 ^{0}C, after which it was allowed to dry at 70 ^{0}C. Finally, the adsorbent was crushed into particles and was then ready for use. The size of the adsorbent particles was measured using a Zetasizer (Malvern Mastersizer 2000) to measure the diameter of the particles.

PAC (SAE2, Pentair-Norit, the Netherlands) was rinsed with demineralized water carefully to remove ash from the PAC surface. The PAC was stored in an oven at a temperature of 100 ^{0}C for one day to remove water. Finally, a sieve (diameter 0.105 mm) was employed to select PAC with diameters > 0.1 mm. Selected PAC was added into the bioreactor.

4.3 Results and discussion

4.3.1 Effect of Taylor bubble on fouling

The impact of the Taylor bubble approach on membrane fouling was evaluated by assessing the TMP increase during step flux experiments applying a sustainable flux flow regime. Results are depicted in Figure. 4.1. Notably, a rapid increase in TMP is observed when applying a liquid flux exceeding 16 L/m^2.h. In order to enhance the effect of Taylor bubble on membrane fouling control, PAC was added to the bioreactor. The effect of PAC additions was minimal or even negligible when the imposed flux was lower than 16 L/m^2.h. However, a clear effect was observed at fluxes exceeding 16 L/m^2.h. Addition of PAC in two different doses, i.e. 1.6 g/L and 10 g/L, gave similar results in terms of TMP build-up during filtration at elevated fluxes. Although PAC clearly shows its positive effect on lowering the TMP, its impact is likely insufficient to cause a breakthrough for enhanced AnMBR operation. It is deduced that PAC only adsorbs a fraction of all foulants causing flux decline. An excessive addition of PAC will not lead to a better sludge filterability than an optimized dose or will even lead to a worse effect, as discovered by other researchers (Akram and Stuckey 2008, Park et al. 1999). The optimized PAC varied in the cited literatures, which may be attributed to the type of raw material and/or manufacturing process of the PAC, as well as the pretreatment of the PAC before dosing. Obviously, also the amount of absorbable foulants will play a role in PAC effectiveness. It is found that a type of PAC (screened by a 100 µm sieve and stored in an oven at 105°C, Pentair-Norit, UK) gave a positive effect at 1.67 g/L but a negative effect at 3.4 g/L (Akram and Stuckey 2008).

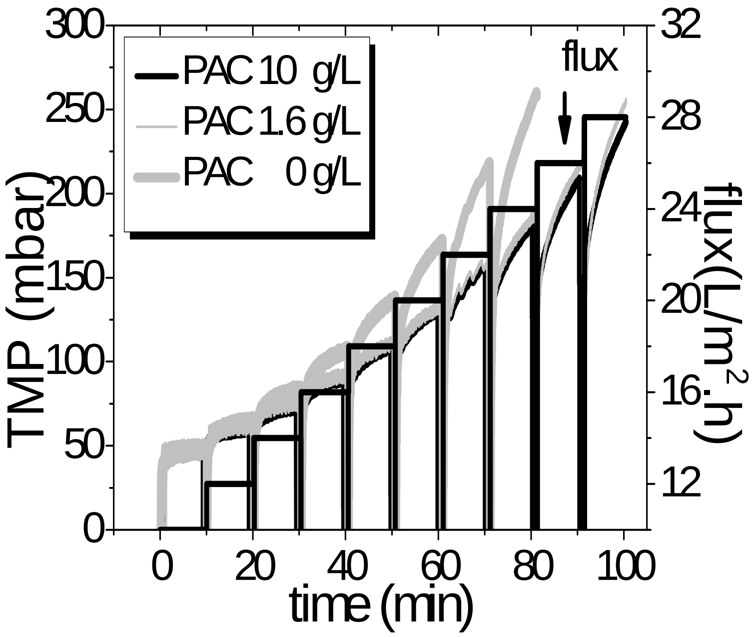

Figure 4.1 TMP versus time

Alternatively, the other type of PAC, with an average size of 100 µm, sieved through 120 × 200 meshes and rinsed several times with ultrapure water to remove inorganic ashes completely, then dried overnight in an oven at 105 °C, and always stored in a desiccator before use (Pentair-Norit SA4, US), did not show a negative effect while PAC dose increased from 1 g/L to 5 g/L (Park et al. 1999). In our here described experiments, the used pretreated PAC did not show a negative effect when a high dose of 10 g/L was used.

4.3.2 Application of magnetic adsorbents

The sludge B, that was derived from the starvation of sludge A, showed an improved filterability, compared to sludge A. As can be seen from Figure 4.2, at the applied flux of 30 L/m^2.h, the TMP corresponding to sludge A quickly increased from 0 to 200 mbar within 1 hour (Fig. 4.2a, 0 g/L, without adsorbent addition). However, the TMP corresponding to sludge B stayed constant at 60 mbar (Fig. 4.2b, 0 g/L, without adsorbent addition). Our results indicate that sludge starvation significantly improved sludge filterability.

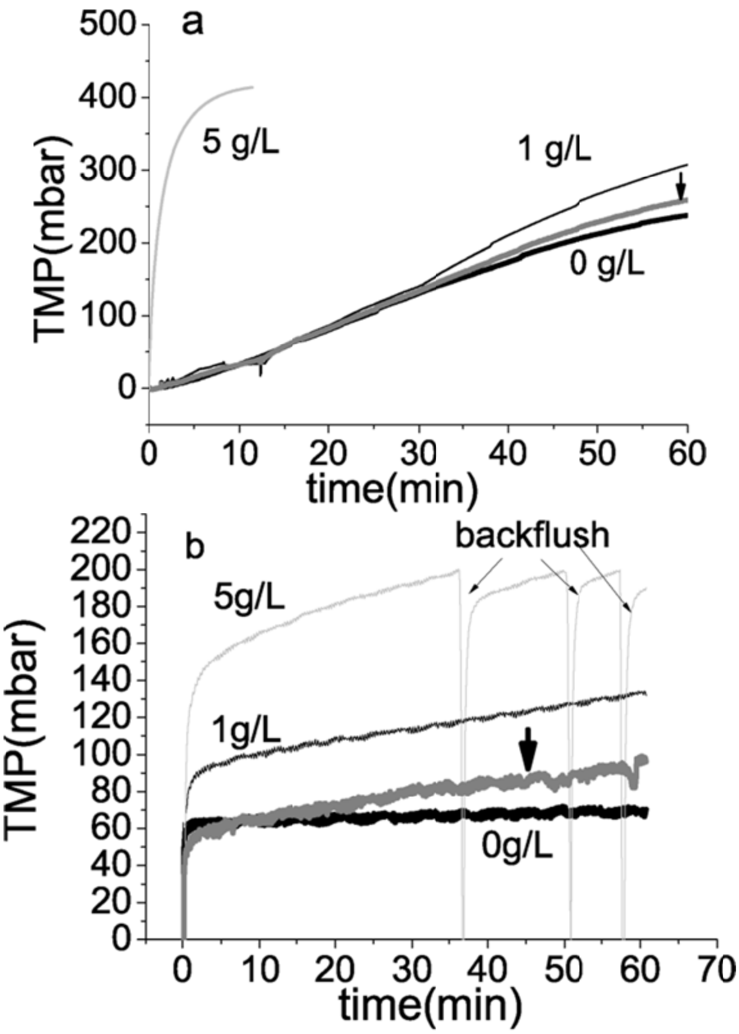

Figure 4.2 TMP versus time for different magnetic adsorbent dosages (flux=30 L/m^{2}h). The bold grey line indicated by arrows represent TMP developing trend after the removal of the adsorbent (5 g/L) from sludge (a: sludge A; b: sludge B)

Generally, the addition of adsorbents in MBRs improves sludge filterability and thus increases the membrane flux (Lohwacharin et al. 2010, Remy et al., Wu et al. 2009). Therefore, the magnetic adsorbent was batchwise added into the completely mixed bioreactor to test its effect on improving the filterability of sludge. The short-term TMP development trends for different adsorbent dosages are also depicted in Figure 4.2. In contrast to expectations, the magnetic adsorbent did not improve the membrane flux, but accelerated membrane fouling, which applied to sludge A and B. A small amount of adsorbent (1 g/L) clearly caused the TMP to increase and the effect was more pronounced when a higher adsorbent dose (5 g/L) was applied. After removing the adsorbent by an external magnetic field, a significant reduction in the membrane fouling trend was observed.

4.3.3 Adsorbent addition, viscosity, and membrane fouling

For reactor operational purposes it is of interest to elucidate why the introduction of this particular adsorbent result in significant membrane fouling. It is normally accepted that high viscosity will result in low filterability. Equation (4-1) can be used to describe the relationship between the feed viscosity and the flux:

$$J = \frac{\Delta p - \Delta \pi}{\eta (R_m + R_r + R_{ir})} \tag{4-1}$$

Where J = flux (m/s); Δp = TMP (Pa); Δπ = osmotic pressure (Pa); η = dynamic viscosity (Pa.s); R_m = membrane resistance (m^{-1}); R_r = reversible fouling resistance (m^{-1}); R_{ir} = irreversible fouling resistance (m^{-1}).

According to Equation (4-1), increasing the viscosity leads to a decrease in achievable flux. The viscosity of anaerobic sludge, with and without adsorbent, is shown in Figure 4.3. The lowest viscosity of concentrated sludge in this Figure is 4.45 mPa.s, which is several times higher than that of clean water and thus possibly limiting the membrane flux in the AnMBR.

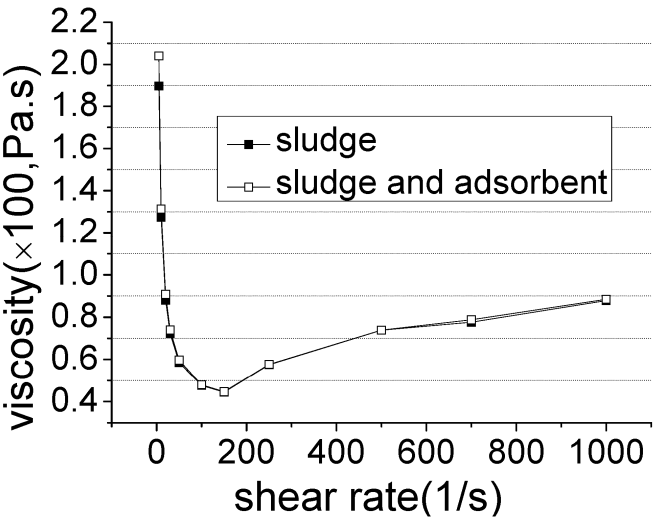

Figure 4.3 Viscosity of concentrated sludge (TSS=40 g/L) and the sludge with adsorbent (5 g/L)

Nonetheless, the short-term experiments (Figure 4.2) indicate a potential membrane flux, reaching 25 L/m^2.h. Furthermore, as can be seen from Figure 4.3, the addition of adsorbent did not lead to a change in the rheological property of the concentrated anaerobic sludge. Although the viscosity did not change, the filterability of the sludge was significantly deteriorated by the addition of the adsorbent, as indicated in Figure 4.3. The adsorbent clearly impacted the filtration process and back-flushing was not able to effectively recover the TMP, which again rapidly increased after back-flushing. Results indicate a low cake permeability that likely can be attributed to the low average particle size of the magnetic adsorbent, i.e. about 1 μm (Figure 4.4b).

Figure 4.4 shows the particle size distributions for the anaerobic sludge and the magnetic adsorbent. Combining results from Figures 4.2 (b) and 4.4, it is postulated that sludge particles whose dimensions fall between 2 and 400 µm do not limit membrane filtration, leading to attainable fluxes of up to 30 $L/m^2.h$.

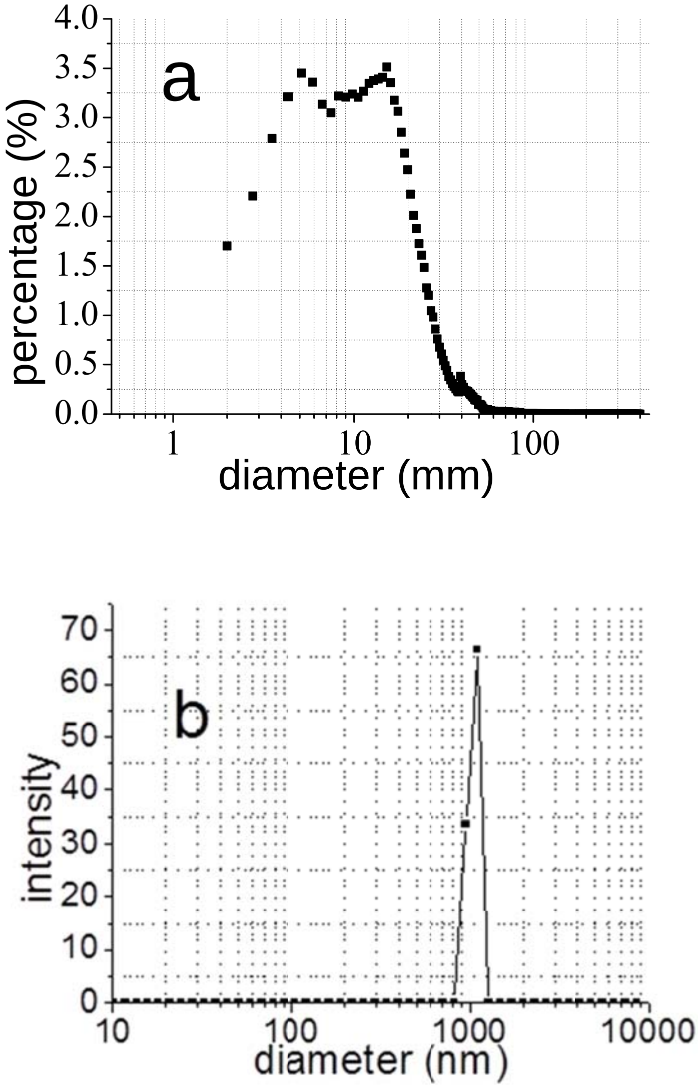

Figure 4.4 Particle size distribution: (a) Anaerobic sludge; (b) Magnetic adsorbent

Apparently, particles <2 µm, i.e. the size range that also includes the magnetic adsorbents, contributed to a drastic flux decline, which is in accordance to other authors (Jeison et al. 2009, Jeison et al. 2008, Jeison and van Lier 2007a, Jeison and van Lier 2007b). The applied slug flow conditions, apparently, could not prevent the accumulation of fine particles on the membrane surface, which subsequently resulted in cake layer compaction. From our results, it is concluded that the magnetic adsorbent with a dimension close to 1 µm has a strong limiting effect on the operation of a membrane under slug flow conditions, even at a concentration as low as 1 g/L. These findings are in agreement with previous work (Jeison et al. 2009, Jeison et al. 2008, Jeison and van Lier 2007a, Jeison and van Lier 2007b).

Figure 4.5 indicates that fine particles in sludge were absorbed by the magnetic adsorbent. As can be seen in Figure 4.5, percentages of particles with sizes around 5 μm increased after the adsorbent addition, likely due to the attachment of fine particles in sludge on the adsorbent surface. However, the addition of the adsorbent also significantly increases percentage of particles with sizes around 1 μm. Therefore, although the magnetic adsorbent adsorbed fine particles, which could be helpful to increase sludge filterability, the total effect was that the addition of the adsorbent decreased the filterability of the sludge due to the addition of the magnetic adsorbent with its size around 1 μm. For magnetic adsorbent particles with a size higher than 1 μm, it is found that gentle mixing can break the big adsorbent into finer adsorbent particles with a size as shown in Figure 4.4 (b). Therefore, after being dosed, an adsorbent with a bigger size may easily break up into smaller sizes in reactors and subsequently act in the same way as an adsorbent with an average size of about 1 μm.

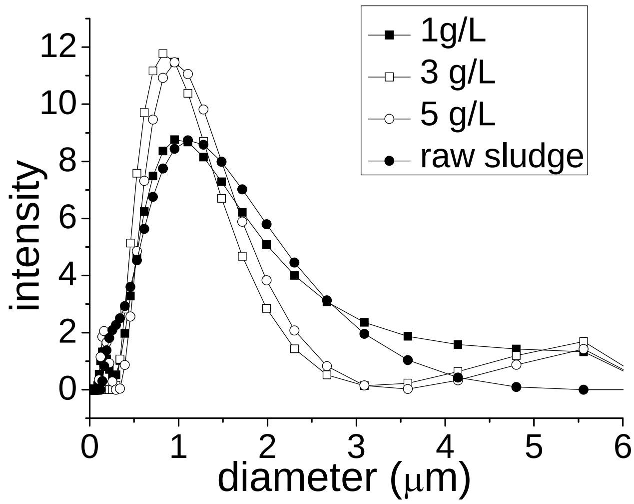

Figure 4.5 PSD in raw sludge supernatant and supernatant with magnetic adsorbent

4.3.4 Sludge losses during adsorbent removal

The applied magnetic adsorbent could not be used to control membrane fouling and/or flux decline because, owing to its average particle size it was acting as a foulant. Nonetheless, if the adsorbent adsorbs large amounts of colloids, which in principle should be possible based on the results depicted in Figure 4.5, the adsorbent could still be useful because it contributes to the reduction of the concentration of foulants and must subsequently alleviate membrane fouling to some extent. Owing to its magnetic character, removal of adsorbent together with the adsorbed colloids is then possible by applying an external magnetic field.

Figure 4.6 Adsorbent in external magnetic field: (left) dry adsorbent; (right) removed from bioreactor

However, the removal of the magnetic adsorbent from the reactor by an external magnetic field was accompanied by the loss of anaerobic sludge, as shown in Figure 4.6 and Figure 4.7. The amount of biomass loss was quantified by decreased TSS and VSS concentrations. As illustrated in Figure 4.7, removing 5 g of adsorbent from the sludge A was accompanied by the loss of 5 g of TSS. The observed sludge loss due to the magnetic adsorbent applied for sludge B was similar (data not shown).

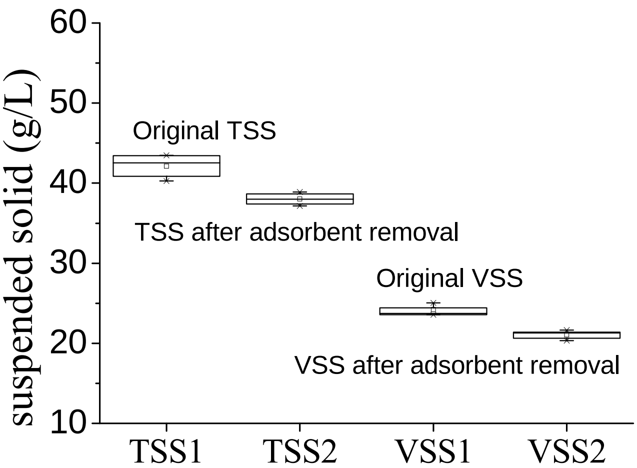

Figure 4.7 TSS and VSS concentration in sludge A before adsorbent dosing and after adsorbent removal

Adsorbent replacement seems to be inevitable during continuous flow operation. After addition of an adsorbent into an AnMBR for controlling membrane fouling, the adsorbent will finally lose its capacity for adsorbing membrane foulants on its surface, concomitantly losing its ability for effective membrane fouling control. Hence, the removal of used adsorbent and the addition of new adsorbent is necessary. During adsorbent removal, sludge loss should be minimized, particularly when bioconversion is dependent on slow-growing microorganisms. Because specific growth rates of microorganisms under extreme conditions such as high salinity are lower compared to more common conditions, sludge loss with adsorbent replacement should be avoided. Based on previous results and discussion, it is concluded that the developed magnetic adsorbent is not very useful for flux control in an AnMBR. Its usefulness depends on its average particle size, prevention of contact with membrane surface, and the possibility to remove the adsorbent without any significant sludge loss.

4.4 Conclusions

In the here used set-up, dosing of magnetic adsorbents to control membrane fouling of anaerobic membrane bioreactor is not satisfactory owing to its negative impact on sludge filterability and the concomitant sludge removal when harvesting the used adsorbents from the reactor. In addition, the use of PAC did not show significant flux improvement. The application of PAC and the magnetic adsorbent in membrane fouling reduction in AnMBR is considered not practical.

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Chapter 5

Shear induced coagulation of fine anaerobic sludge particles

Chapter 5 Shear induced coagulation of fine anaerobic sludge particles

Abstract
In Chapter 4, it was found that dosing adsorbents could not bring about a significant membrane fouling reduction. Therefore, the effort of modifying sludge filterability was directed to the application of coagulants. In order to explore the feasibility of using sodium ions as coagulant, the feasibility of using shear-induced coagulation to increase the sizes of fine particles in sludge in anaerobic membrane bioreactors was investigated. The large number of sodium ions in saline wastewaters can suppress the zeta potential of fine particles in water, thereby acting as a coagulant and possibly even making it unnecessary to add any external coagulant. For our investigations, supernatant with a high concentration of fine particles was obtained from an AnMBR and transferred into jars in which magnetic stirrers were used for mixing. Results revealed that high concentrations of sodium ions (>10 g Na^+/L) significantly increased the size of particles in the supernatant as a result of the repulsive free energy between charged particles being greatly suppressed by the sodium ion. Further experiments confirmed that shear-induced coagulation was significant, even in anaerobic sludge with a high concentration of total suspended solids (40 g/L). A stirring time of 20 minutes was sufficient to achieve considerable coagulation. Computational fluid dynamics showed that the stirring effect was quickly dispersed in the jar due to the high viscosity of the sludge, indicating the importance of an effective mixing tank design if a high degree of coagulation is to be achieved.

5.1 Introduction

Colloids are known to contribute to membrane fouling in bioreactors, which is a problem that needs to be addressed (Gustafsson et al. 1996, Jonsson and Jonsson 1996, Kim and Hoek 2002). While membranes obviously retain particles whose diameters are larger than those of the membrane pores, smaller particles (sometimes 10 to 1000 times smaller than the pore size) can also be retained (Stumm and Morgan 1996) and then accumulate on the membrane surface. Colloids are the main foulants in anaerobic membrane bioreactors (Choo and Lee 1996). Jeison (2007) found that both anaerobic sludge and the supernatant obtained by centrifuging the sludge have the capacity to foul a membrane (Jeison 2007). However, this capacity is strongly dependent on particle size because inertia-induced lift forces make it much easier for large particles to be carried away from a membrane surface (Song and Elimelech 1995). It is therefore desirable to increase the size of fine particles in anaerobic bioreactors, as a means of preventing membrane fouling.

The sizes of particles can increase as a result of coagulation; suitable shear conditions and the presence of positively charged ions can play a role in colloid coagulation, possibly making it unnecessary to add any further coagulant. Colloids are normally stable due to an electric surface charge that prevents small colloids from becoming bigger. Fine particles in water can be encouraged to combine into larger aggregates by the addition of a coagulant. Even in the absence of a coagulant, however, fine particles (colloids / nanoparticles) can collide and form larger particles under conditions of low shear stress; this is known as shear-induced coagulation (Chin et al. 1998, Flesch et al. 1999, Mietta et al. 2009, Spicer et al. 1996, Spicer and Pratsinis 1996). Chin et al. (1998) reported that nanoparticles can even become larger than the colloid size range without any use of coagulants. The presence of Na^+ ions can lead to a significant reduction in residual turbidity by suppressing electric double layers of particles (Stumm and Morgan 1996), and can therefore contribute to coagulation. It remains unclear, however, whether bio-colloids, which are colloids generated in bioprocesses, can be coagulated by shear-induced coagulation alone. If bio-colloids can become larger as a result of shear-induced coagulation this process could contribute significantly to the development of anaerobic membrane bioreactors (AnMBR) addressing the membrane fouling problem, particularly in saline wastewaters where the large amount of sodium would also act as an inherent natural coagulant.

The phenomenon of coagulation can be partially explained by the DLVO theory, according to which the free energy between two charged spherical particles (Birdi.K.S. 2009, Pashley 2004) is given by:

$$V_t = V_r - V_a = 2\pi\varepsilon a\varphi^2 e^{-\kappa s} - \frac{Aa}{12s} \qquad (5\text{-}1)$$

in which

$$\kappa = \sqrt{\frac{1000e^2 N_A}{\varepsilon_0\varepsilon_r kT}\sum z_i^2 M_i} \qquad (5\text{-}2)$$

Where V_t = total free energy between spherical colloids (J); V_r = repulsive free energy (J); V_a = van der Waals interaction energy (J); a = particle radius (m); φ= zeta potential (V); κ = reciprocal of Debye length (m^{-1}); A = Hamaker constant (J); s = distance between two spherical particles (m); ε = permittivity, equal to $\varepsilon_0\varepsilon_r$ where ε_0 = permittivity of free space (F/m) and ε_r = the dielectric constant; k = Boltzmann constant (J/K); T = absolute temperature in kelvins (K); N_a = Avogadro number (mol^{-1}); e = charge (C); M_i = concentration of component i (mol/l); and z_i = valence of component i.

The total free energy between spherical colloids plays an important role in coagulation. Effective coagulation can be achieved by realizing low total free energy. It is far from clear whether shear-induced coagulation can produce significant coagulation of the colloids in anaerobic membrane bioreactors. According to equations (5-1) and (5-2) above, van der Waals interaction energy relies on the Hamaker constant, whereas repulsive free energy does not. The Hamaker constants for materials in water are between 0.1×10^{-20} and 10×10^{-20} J (Hsu 2000). Materials whose optical properties are close to those of water have low Hamaker constants, while metals and all kinds of oxides have higher Hamaker constants (close to 10×10^{-20} J and 1×10^{-20} J, respectively) than the water-like polymers. Thus, the fine particles investigated in previous research (Chin et al. 1998, Flesch et al. 1999, Spicer and Pratsinis 1996) have higher Hamaker constants than the bio-colloids (e.g. 0.3×10^{-20} J (Choo and Lee 1998)). A low Hamaker constant leads to a low van der Waals interaction energy, which is not favorable for coagulation. It therefore remains unclear whether significant coagulation of bio-colloids can occur under low shear conditions.

We therefore investigated the extent of shear-induced coagulation in bio-colloids that had been generated in anaerobic membrane bioreactors. The improvement in shear-induced coagulation due to the addition of sodium ions was also tested. Further experiments were carried out to test the effect that a high concentration of solids in sludge had on shear-induced coagulation. Finally, the hydraulic conditions during the shear-induced coagulation were characterized using computational fluid dynamics (CFD)

5.2 Methods and materials

A lab scale AnMBR setup is shown in Figure 1.1 (left). The operation of AnMBR has been presented in chapter 2. The reactor had been operated for one year before the start of these experiments. The supernatant, which contained a large number of colloids, was taken from the anaerobic membrane bioreactor after the reactor's operation had been temporarily halted and the sludge allowed settling overnight.

The characterization of the rheological properties of the sludge is described in Chapter 4. A Malvern Zetasizer (nano-series) was used to determine the zeta-potential and conductivity of the colloids in the supernatant under different salinities. The particle size measurement is explained in Chapter 4. A 6-position magnetic stirrer (5 mm in length and 3 mm in diameter: model LD-746 from Labinco BV, The Netherlands) was used for mixing 200 ml of supernatant in a 250 ml jar.

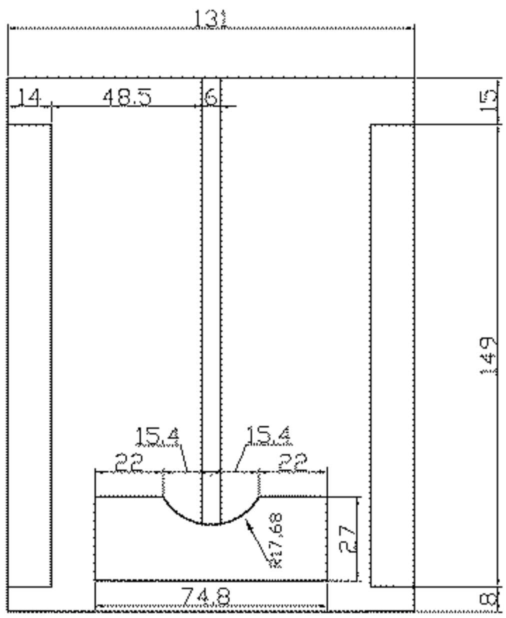


Figure 5.1 Dimensions of the mixing jar used for the coagulation of anaerobic sludge (mm)

As well as the supernatant, a 250 mL jar was also filled with anaerobic sludge (TSS= 40 g/L) and then mixed. Four evenly spaced baffles were attached to the wall of the jar, the dimensions of which can be found in Figure 5.1. The hydraulic conditions in the jar during mixing have been characterized by computational fluid dynamics. A gridded three-dimensional jar and a stirrer whose dimensions were identical to those represented in Figure 5.1 were drawn (GAMBIT version 2.2.30) and then incorporated into FLUENT software (version 6.3.26) to obtain a description of the flow field in the jar during coagulation. The modeling procedure used was the steady turbulent model.

Steady turbulent model

A steady pressure-based realizable k-ε turbulent model with wall enhancement treatment was used to describe the turbulent condition in the jar. The realizable k-ε model performs better than the Standard and RNG k-ε turbulent models for flows involving rotation, boundary layers under strong adverse pressure gradients, separation, and recirculation. A detailed description of the realizable k-ε turbulent model can be found in previous publications (Shih et al. 1995).

Material property

A universal dynamic spectrometer was used to determine the rheological properties of the anaerobic sludge, which is a non-Newtonian fluid. These rheological properties were then incorporated into the model using the User Defined Functions provided in the FLUENT program to extend its function.

Boundary conditions

For boundary conditions, a multi-reference frame was used in the modeling. The impellers and nearby cell zones were assigned to a moving reference frame (30 rpm) in the modeling, while other cell zones in the interior and on the wall of the jar were stationary. The shaft rotated with the same speed.

Solutions control

The FLUENT software derives modeling results by solving conservation equations on the basis of the Eulerian model theory. The conservation equations are solved for each domain (i.e. for each cell). In the modeling, a pressure-velocity coupling method (SIMPLE), which is suitable for steady state modeling, was used for pressure-velocity coupling. SIMPLE uses the corrections between velocity and pressure to obtain the pressure field. The conservation equations are solved by discretization. In the modeling, Standard and First Order Upwind methods corresponded to pressure and momentum discretization, respectively. The latter discretization method was also used for turbulent kinetic energy and turbulent dissipation rate discretization.

The initial values for gauge pressure and velocity were absolute zero. For the initial turbulent kinetic energy and turbulent dissipation rate, 0.001 m^2/s^2 and 0.01 m^2/s^3 were used, respectively.

Model verification

It is difficult to verify the accuracy of the modeling strategy. Verification based on tracer experiments cannot perfectly match the CFD model (the relative error was 20%) (Ding et al. 2010). In addition, verification of CFD modeling based on dosing tracer and later retention time comparison is impossible if there are no influent and effluent for the zone being modeled, e.g. jar test in this study.

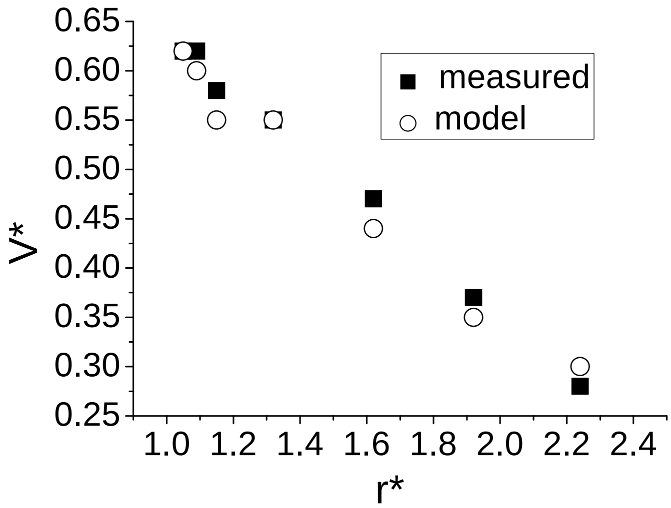


Figure 5.2 Velocity variations along the center-line of the impeller disc, V* = radial velocity

Particle Image Velocimetry (PIV) can provide vivid pictures of a flow field that can then be used to verify a CFD model. However, anaerobic sludge with high TSS concentration is so dark that the PIV becomes useless. In view of these limitations on verification, the above modeling strategy was verified by comparing Kusters' experimental results (Kusters 1991) with the modeling outcomes that derived from the same modeling procedure (see Figure 5.2). Our modeling strategy appears to provide a reasonable simulation of Kusters' results, as shown in Figure 5.2. By changing the dimensions of the jar in Kusters' experiments and using sludge instead of water, we obtained the CFD model that was used to depict the hydraulic conditions in our experiments. It is considered that this modeling strategy can also provide a reasonable simulation of the jar test in this study.

5.3 Results and discussion

5.3.1 Suppressing double electric layer by Na^+

Effect of Na^+ concentration on the zeta potential and total energy reduction

Figure 5.3 shows the relationship between Na^+ concentration and the zeta potential of particles in the supernatant, and conductivity. The zeta potential of particles increased linearly from -24.1 mV to -15.7 mV as the Na^+ concentration increased from 2 g/L to 8 g/L. The conductivity increased linearly as the concentration of sodium increased from 2 g/L to 10 g/L. The measurement of zeta potential at sodium concentrations of 10 g/L and higher was not reliable. Linear extrapolation of the zeta potential regression line yields a zeta potential of -12.77 mV at 10 g Na^+/L, indicating that the zeta potential was increased by around 50% compared to that for a Na^+ concentration of 2 g/L. As indicated in equation (5-1), a 50% decrease in zeta potential can lead to a decrease of about 75% in repulsive energy. This sharp decrease in repulsive energy is very helpful in reducing the energy barrier when two fine particles approach each other, which makes it easier for small particles to combine after colliding.

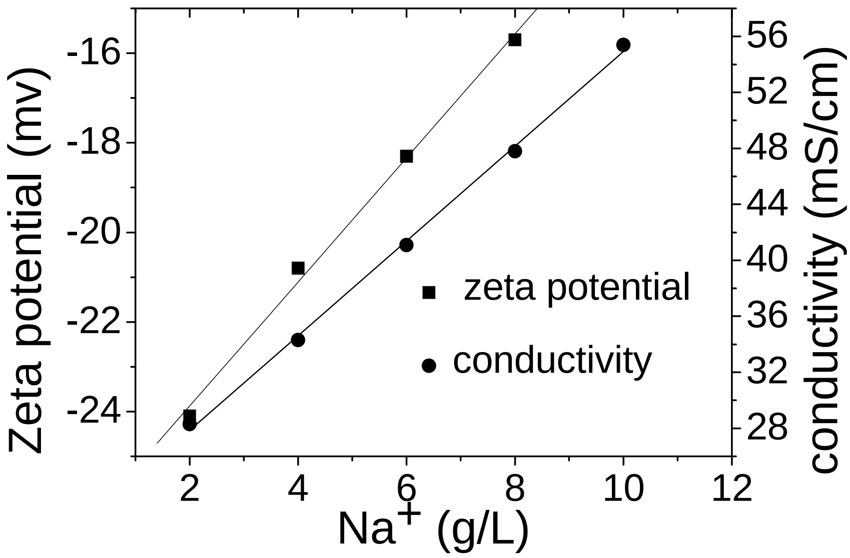
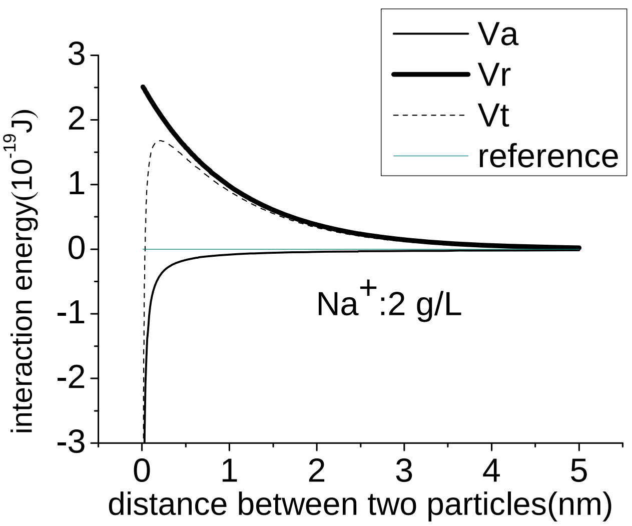


Figure 5.3 Conductivity and zeta potential of anaerobic particles

Effect of Na^+ concentration on free energy

In order to determine a potentially effective sodium concentration for achieving significant coagulation, three energies between two particles were calculated on the basis of equations (5-1) and (5-2), and are depicted in Figure 5.4.



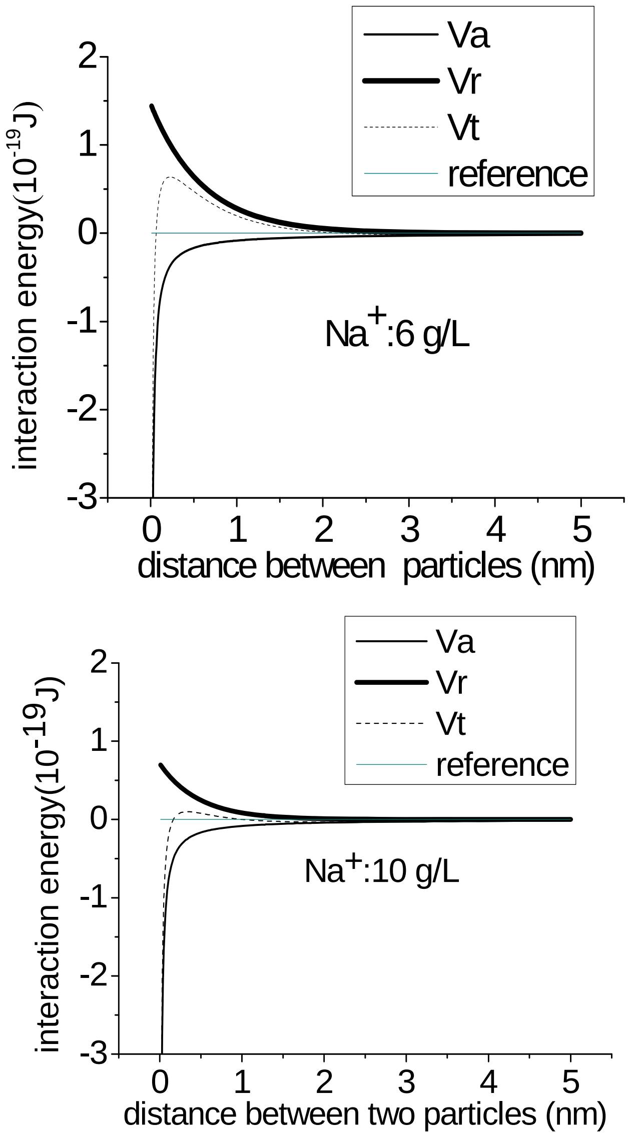


Figure 5.4 Electrical repulsive and van der Waals attractive forces at different Na^+ concentrations; $A=0.1\times10^{-20}$ J; $a=100\times10^{-9}$ m

As stated previously, the zeta potential of particles increased linearly from -24.1 mV to -15.7 mV when sodium concentrations increased from 2 g/L to 10 g/L. The particle diameter was 100×10^{-9} m and the Hamaker constant was 0.1×10^{-20} J. These data were used to calculate free energy variation. Figure 5.4 shows that the total free energy reduced significantly as the sodium ion concentration increased. The energy barrier was reduced from around 1.7×10^{-19} J to around 0.2×10^{-19} J while the Na^+ concentration increased from 2 g/L to 10 g/L. The 88% decrease in the energy barrier created a sufficient opportunity for two small particles to overcome the energy barrier and, in this way, to increase particle diameters under suitable mixing conditions.

5.3.2 Effects of mixing and salt on particle size distribution

Non-saline conditions

Jar tests were performed to test the effects of different shear conditions on coagulation under non-saline conditions. Table 5.1 shows the number of particles in the supernatants before and after the supernatants had been mixed for 180 minutes to guarantee a stable particle size distribution. Numerous fine particles were present in the supernatants; these fine particles are suspected of blocking membrane pores leading to membrane fouling during membrane operation. Even the gentlest mixing did not significantly decrease the number of fine particles, which may be at least partially attributable to the low Hamaker constant, representing a low attractive energy. More vigorous mixing clearly did not offer good effect. Even though the mixing applied could be expected to have provided sufficient opportunities for these fine particles to collide, the non-saline conditions did not provide a significant coagulation at different mixing conditions.

Table 5.1 PSD in supernatant anaerobic MBR under various mixing conditions

	Number of particles before and after mixing ($\times 10^{08}$)				
Particle diameter(µm)	Original sample.	125 rpm	250 rpm	375 rpm	500 rpm
>0.15 and <0.4	5.75±0.31	5.34±0.13	5.87±0.21	5.98±0.14	6.01±0.33
>0.5 and <5.0	4.32±0.22	3.92±0.15	4.57±0.18	4.62±0.20	4.49±0.15

Errors obtained by 8 detections

Saline conditions

Sodium (10 g/L as Na^+) was added into the supernatant to test the effect that extra saline conditions have on coagulation. Only the gentlest mixing (125 rpm) was used because, as indicated in equation (5-3) below (Hsu 2000), a low velocity gradient leads to a larger average particle diameter (Chin et al. 1998, Flesch et al. 1999, Spicer and Pratsinis 1996):

$$d = \alpha G^{-\gamma} \quad (5\text{-}3)$$

Where d = the average diameter of floc, m; G = velocity gradient, s^{-1}; α = constant, m/s; and γ = constant, non-dimensional,

Figure 5.5 shows that the addition of a large quantity of sodium significantly improved the shear-induced coagulation: the total number of particles (0.15 µm < d < 0.40 µm) was reduced by 40%, while the number of large particles (d > 0.5 µm) increased. It was found that particles in the range of 0.1 to 0.4 µm were responsible for the membrane fouling (Geilvoet 2010). It is therefore evident from Figure 5.5 that a high concentration of Na^+ may be useful in alleviating the problem of membrane fouling.

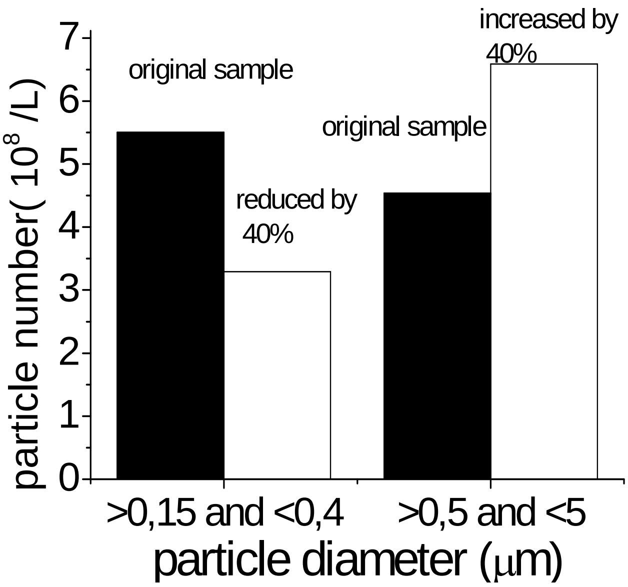


Figure 5.5 PSD in supernatant from anaerobic MBR (Na^+, 10 g/L), 125 rpm

Although significant coagulation was achieved with saline conditions in the supernatant, it remains uncertain whether a good degree of coagulation can also occur in the sludge in membrane bioreactors, given the same mixing and the same saline conditions. The uncertainty derives from the higher TSS concentrations in sludge than that in the corresponding supernatant, as is explained below.

Collisions between fine particles and the fragmentation of large particles can either decrease or increase the number of fine particles. Fine particles may effectively disappear by forming larger particles as a result of collisions, or alternatively, fine particles can be produced through the fragmentation of larger particles. The orthokinetic collision frequency and fragmentation rate during coagulation (Saffman and Turner 1956) are given by:

$$\beta = 1.294\left(\frac{\varepsilon_h}{\eta}\right)^{\frac{1}{2}}(R_i + R_j)^3 \qquad (5\text{-}4)$$

$$S_i = \left(\frac{4}{15\pi}\right)^{\frac{1}{2}}\left(\frac{\varepsilon_h}{\eta}\right)^{\frac{1}{2}}\exp\left(-\frac{\varepsilon_c}{\varepsilon_h}\right) \qquad (5\text{-}5)$$

Where β is the coagulation collision frequency; S_i is the fragmentation rate; ε_h is the homogeneous turbulent energy dissipation rate in a stirred tank; η is the kinematic viscosity of the suspending fluid; R_i is the radius of particle i; R_j is the radius of particle j; and ε_c is the critical turbulent energy dissipation rate at which the aggregates fragment.

Equation (5-4) indicates that sludge with a high TSS concentration provides higher collision frequencies than its supernatant. This is because sludge generally has a greater number of large particles than the corresponding supernatant and the existence of large particles means a greater collision frequency. Hence, if sludge and its supernatant are both involved in coagulation under the same conditions, the collision frequency for fine particles should be higher in the sludge than in the supernatant. Kusters (1991) also found that an increase in solids concentration leads to an increase in the average aggregate size. Unfortunately, however, the solids concentration in his experiments (i.e. 2 g/L) was much lower than solids concentrations in normal membrane bioreactors and his results can, therefore, not yet be safely extrapolated to sludge with a far higher solids concentration.

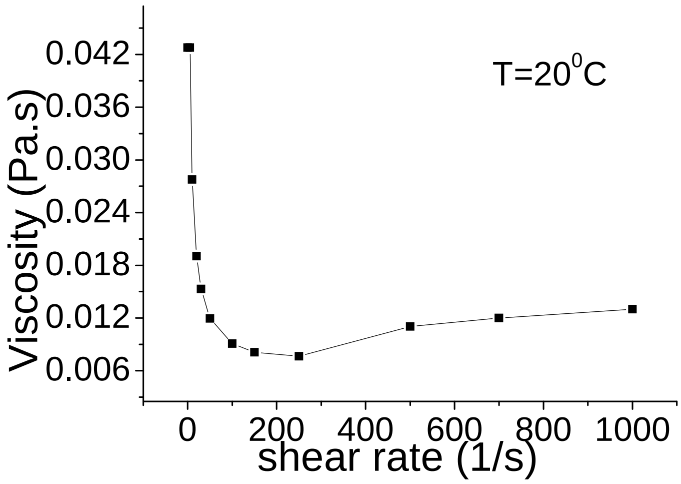


Figure 5.6 Viscosity of anaerobic sludge (TSS = 40 g/L)

High solids concentrations in sludge may play a positive role in shear-induced coagulation, as explained above. On the other hand, the high viscosity that results from a high solids concentration may play an obscure role. Anaerobic sludge with a high TSS concentration can be very viscous compared to clean water, as indicated in Figure 5.6: the viscosity for a TSS of 40 g/L ranged from 7×10^{-3} to 42×10^{-3} Pa.s, whereas the viscosity of clean water is only 0.7225×10^{-3} Pa.s at the same temperature. Equations (5-4) and (5-5) indicate that high viscosity leads to a decrease in collision frequency and a lower fragmentation rate, making it difficult to predict the effect that viscosity will have on coagulation.

To test the results of this theoretical analysis, practical experiments were carried out to verify whether a significant coagulation effect could be achieved under saline conditions with a high sludge concentration. Anaerobic sludge (800 ml, TSS: 40 g/L) was placed into a 2.5 L jar in order to test whether shear induced coagulation could occur. Since the sludge started to settle when the rotation speed of the stirrer dropped below 10 rpm, the rotation speed was set to 30 rpm in order to ensure complete suspension of the sludge. Figure 5.7 demonstrates that the number of particles whose diameters were between 0.25 μm and 0.4 μm decreased from 3.01×10^{8} to 8×10^{6} in 10 minutes, but no subsequent decrease in the particle numbers occurred. Figure 5.7 confirms that shear-induced coagulation occurred in saline conditions despite the high TSS concentration.

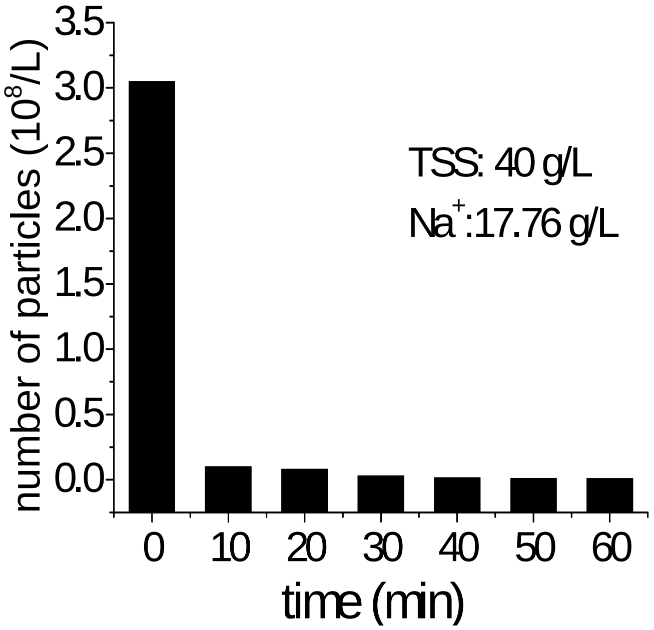


Figure 5.7 Variation in the number of particles with time (diameter: 0.25 μm - 0.4 μm); 30 rpm

5.3.3 Hydraulic conditions in the mixing tank

In order to achieve a good coagulation effect (i.e. as shown in Figure 5.7) the design (shape and size) of stirrers is important, especially when the liquid viscosity is high. The high viscosity may result in the mixing effect disappearing quickly within a small distance, allowing other areas further away to avoid being stirred at all. Shear-induced coagulation may therefore not be significant on large scales despite the good coagulation shown in the jar tests. Figure 5.8 provides a graphic portrayal of the velocity distributions within a mixing tank. Three sections were selected to describe the velocity difference at different levels of the mixing tank. As can be seen in Figure 5.8, the velocities near the stirrer were generally higher than those at the top and bottom of the mixing beaker The stirrer clearly had less influence at the top and bottom of the jar indicating the importance of the number and design of stirrers if a good coagulation in sludge is to be achieved on a large scale.

The distribution of shear stress in the mixing tank is also of interest. A high velocity gradient is good for enhancing the frequency of particle collisions, but also leads to high shear stress that can break up particles. Figure 5.9 shows that the highest shear stress occurred at the contact with the stirrer. Most of the material in the mixing tank, however, experienced only low shear stress. Hence, low velocity gradients dominated in the jar and contributed to the significant fine particle coagulation in this study.

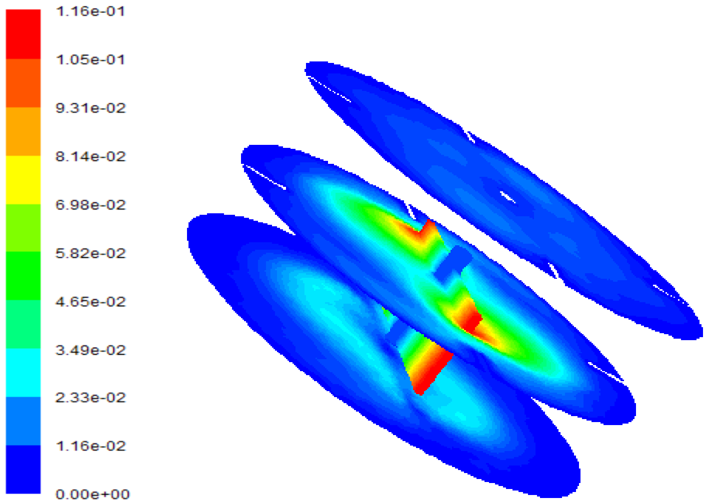


Figure 5.8 Velocity (m/s) distribution in sections perpendicular to the stirrer at three different levels (30 rpm); blue low velocity, red high velocity

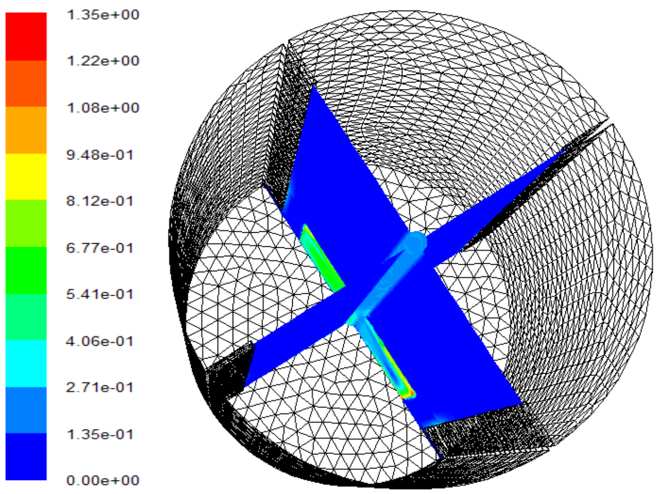


Figure 5.9 Distribution of shear stress (Pa) on two sections and on the stirrer surface (30 rpm); blue low shear stress, red high shear stress

5.4 Conclusions

Significant coagulation effects were observed in anaerobic supernatants in which the sodium ion concentration was as high as 10 g/L. Significant coagulation of fine particles was also found to occur in anaerobic sludge under hyper-saline conditions, despite a high TSS concentration of 40 g/L. Most fine particles quickly disappeared (within 20 minutes) when the anaerobic sludge was coagulated.

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Chapter 6

Membrane fouling in an anaerobic membrane bioreactor under high salinity conditions

Chapter 6 Membrane fouling in an anaerobic membrane bioreactor under high salinity conditions

Abstract
In chapter 5, it was found that the size of colloidal particles could increase under the applied shear and salinity conditions. The number of small-sized colloidal particles decreased significantly, which provided a possibility to use a suitable shear to induce coagulation for controlling membrane fouling under saline conditions. In order to verify the feasibility of using high Na^+ concentrations, naturally existing in some wastewaters, as a coagulant to control membrane fouling, we investigated the membrane fouling phenomenon in an anaerobic membrane bioreactor under high salinity conditions. A multi-bladed stirrer was installed in the reactor, which aimed at providing a good mixing condition for inducing coagulation. The rotation speed of the stirrer was set at 30 rpm for achieving the coagulation effect. A sludge was cultured in a saline environment with sodium concentration as high as 17 g/L. A non-saline sludge was also applied at the same conditions for comparison. The salinity of the non-saline sludge was increased from 0 Na^+ g/L to 10 Na^+ g/L and finally to 20 Na^+ g/L. We observed that, under the applied conditions in the non-saline sludge, the increase in salinity could contribute to membrane fouling control. Under the same conditions, while flux was maintained at 15 $L/m^2.h$, TMP increased more quickly when the saline sludge was used. Apparently, both the sodium induced coagulation and the applied shear were insufficient to control membrane fouling in the AnMBR treating saline wastewater. It is postulated that sodium was a too weak coagulant for the saline sludge, likely because much longer reaction times are required for reaching a stable particle size.

6.1 Introduction

A high amount of organically polluted salty wastewater is discharged every year. The problems that arise when the wastewater is treated by means of conventional biological methods include high effluent suspended particles and low pollutant removal efficiencies. These problems may be addressed by combining membrane technology and bioreactor technology, since membrane separation ensures full retention of the biocatalysts, while membrane permeate is free of suspended solids. Considering the advantages of anaerobic technology for treating high strength wastewaters (van Lier 2008), the impact of salinity on anaerobic membrane bioreactors is further investigated.

Owing to the selective accumulation of small particles on the membrane surface, membrane fouling reduction is the prime concern in operating AnMBR systems (Cui et al. 2003, Meng et al. 2009). High shear stress can be effective in shifting small particles from the membrane surface to the bulk solution, but the high shear stress also results in smaller particles, which may decrease sludge filterability and anaerobic conversion efficiency (Jeison et al. 2009). Currently, several methods are under research, such as coagulation, to reduce the number of small particles in the membrane tank and thus enhance membrane fouling control. Coagulation is an effective method for increasing the size of potential foulants in (An)MBR systems, preventing the loss of cake layer permeability and thus maintaining a high operational membrane flux.

Membrane fouling generally can be classified into three categories: i) biofouling due to the deposition, attachment, and growth of bacteria cells or flocs on membrane surface; ii) organic fouling due to the deposition of SMP and/or EPS; iii) inorganic fouling. In (An)MBR research, biofouling and organic fouling are more addressed compared to inorganic fouling (Meng et al. 2009). With regard to AnMBRs, anaerobic biomass produces higher amounts of EPS and/or SMP under high salinity conditions (20 g NaCl/L and 40 g NaCl/L) compared to non-saline environments (Vyrides and Stuckey 2009a, b). Because EPS and/or SMP has been identified as key parameter in membrane fouling, AnMBRs are expected to suffer from low sludge filterability when operated under saline conditions compared to non-saline conditions, while membranes retaining the high molecular weight compounds in the bioreactor (Vyrides and Stuckey 2011, 2009c). Inorganic fouling is due to chemical crystals formation and precipitation on membrane surface and membrane pores or to the interaction between biopolymers and ions that may form a dense cake layer (Meng et al. 2009). In addition to organic fouling, inorganic fouling may play a significant role in membrane fouling when an (An)MBR is operated under saline conditions, particularly when multivalent cations are present.

Na^+ plays an important but contradictive role in membrane fouling. On the one hand, salt has a significant negative impact on overall membrane permeability in aerobic membrane bioreactors even at relatively low salt concentrations of 4 g/L (Reid et al. 2006a). During continuous operation, the treatment of saline wastewater requires more frequent membrane cleaning than the treatment of fresh wastewater (Tam et al. 2006). Faibish et al. (1998) described that permeability and porosity of the cake layer generally decrease when the ionic strength increases.

Some reasons have been proposed to explain the negative effects of Na^+ on membrane fouling. Firstly, which particularly calls for reverse osmosis membranes, the effective driving force is reduced due to concentration polarization and thereby hydraulic resistance is increased (Lay et al. 2010). Secondly, higher salt concentrations would result in greater scaling propensity and aggravate colloidal fouling due to super-saturation and double layer compression in cake layers (Lay et al. 2010). Thirdly, higher salt levels would increase SMP level (Reid et al. 2006b). On the other hand, saline water could effectively clean fouled membrane by gel layer swelling and ion-exchange reaction (Lee and Elimelech 2007). Therefore, Na^+ can act as a fouling promoter but also as a cleaning agent.

Alternatively, Na^+ may be used to promote coagulation as a means of reducing membrane fouling (see also Chapter 5). Fine particles in bioreactors are negatively charged (Ramesh et al. 2006) and Na^+ can suppress the electric double layers of these particles (Stumm and Morgan 1996). As explained in Chapter 5, under suitable mixing conditions, coagulation can occur despite the absence of an externally added coagulant that is normally a multi-charged polymer or a multi-valent cation. For instance, it is reported that turbidity could be significantly reduced by the presence of Na^+ (Stumm and Morgan 1996). Therefore, it is of great interest to examine whether and when the presence of Na^+ can lead to big particle formation in wastewater treatment by (An)MBR, and thereby enhancing the sludge filterability.

It is postulated that Na^+ promotes the formation of dense cake layers when a reactor is not well mixed, whereas, by providing mixing for good coagulation, the fouling may be alleviated to some extent. Therefore, in order to verify the feasibility of using high Na^+ concentrations naturally existing in saline wastewaters as a coagulant to control membrane fouling, an AnMBR equipped with a multi-blade stirrer to provide optimal mixing conditions was designed and tested, and the cake layer was analyzed.

6.2 Methods and materials

Filtration operation

A 4.5 liters AnMBR was operated in a gas-lift mode, using either high salinity adapted anaerobic sludge or fresh sludge as inoculum. Biogas recirculation was applied using a gas pump (Watson Marlow 323 D) and then injected into a tubular membrane (Pentair-Norit, Enschede, the Netherlands), with 5.2 mm in diameter and 0.74 m in length, pore size 30 nm. The superficial velocity of the gas in the tubular membrane was 0.74 m/s, and the induced slug superficial velocity was 0.34 m/s. The inner diameter of the bioreactor was 10 cm. A shaft was placed in the bioreactor for mixing. Eleven blades were evenly distributed along the shaft. The size of each metal blade welded on the shaft was 60 mm × 20 mm. The distance between two consecutive blades was 30 mm. Four baffles (580 mm × 10 mm) were evenly distributed along the rim of the bioreactor to improve mixing. The rotation speed of the shaft was maintained at 30 rpm in order to induce coagulation. Figure 6.1 shows a schematic view of the bioreactor. TMP was measured by means of a pressure sensor (AE sensor, serial number: 261920). The signals from the pressure sensor were recorded using Labview software. The membrane was back flushed with a flux equal to 200 $L/m^2.h$ for 6 seconds at every 10 minutes. In addition, when the TMP reached 200 mbar due to membrane fouling, back flush was also launched automatically to reduce TMP.

The saline and the non-saline sludge

A saline sludge was obtained from an expanded granular sludge bed (EGSB) wastewater treatment plant (Shell Moerdijk, The Netherlands), treating high salinity wastewater for more than 10 years (Ismail et al. 2010). This wastewater contained a sodium concentration in the range 10–15 g/L, and the sludge was already adapted to this high salinity. However, the sodium concentration in the saline sludge at the moment of sampling was 17 g/L. It is clear that this is much higher than those found in conventional non-saline sludges. Non saline anaerobic sludge was obtained from an EGSB reactor treating lactose wastewater (Purac Biochem, Gorinchem, The Netherlands). Prior to inoculation, the granular non-saline sludge was crushed using a sieve with pore size of 0.45 mm.

Both sludges were allowed to adapt to the experimental conditions for over 4 months. The substrate consisted of gelatin: acetate: propionate: butyrate = 2:1:1:1 on chemical oxygen demand (COD) basis, whereas the organic load of the reactor was 0.1 g COD per g volatile suspended solids (VSS) per day. HRT was 96 hours and no sludge was withdrawn in the adaptation period. The adaptation period was used to minimize the influence of the previous environmental conditions in respective full scale reactors on the present experimental study. Sodium chloride was added to the substrate to maintain the high salinity in the bioreactor in which the saline sludge was cultured. In the feed of the non-saline sludge, high salinity was not applied. Therefore the salinities of the two sludges were constant in the adaptation period. After the adaptation period and during the experiments, the salinity of the saline sludge was not changed, whereas the salinity of the non-saline sludge was increased step by step to test the influence of salinity on sludge filterability. The increase in salinity of the non-saline sludge and the filtration of the non-saline sludge were performed within 2 hours.

Analysis

Particle size distribution (PSD) was measured using a particle counter (Hiac Royco Model 3000). With the same instrument, environmental scanning electron microscope (ESEM) was performed for visualizing the cake layer on the membrane. Without any pre-treatment the membrane samples for the ESEM analysis were put into the instrument and the ESEM could analyze samples in their original forms. Vacuum was created before the analysis. Fourier transform infrared spectroscopy (FTIR, Spectrum 100 FTIR Spectrometer) was used to characterize functional groups of the foulant on the membrane surface. Functional groups in the compounds present in the cake layer correspond to specific wave lengths. By matching of the observed wave lengths, functional groups of the compounds present in the layer can be identified.

Particle size and zeta potential measurement

An experiment was performed to verify the existence of shear-induced coagulation in the saline sludge. At the start of the experiment the rotation speed of the stirrer was increased to 100 rpm. Later, the rotation speed was reduced to 30 rpm to allow small particles to form bigger particles. The particle size measurement of submicron particles and the measurement of zeta potentials of colloids are described in Chapter 4 and Chapter 5, respectively. The zeta potential of the colloids linearly increased from -24.1 mV to -17.8 mV while sodium concentration increased from 2 g/L to 10 g/L. The Malvern Zetasizer started to give unreliable results when the sodium concentration was higher than 10 g/L. Therefore, measuring zeta potential at higher sodium concentrations was not performed.

Mixing in the reactor

Effective mixing is important for achieving good coagulation. This requires a good design of shape and size of the applied stirrer. The viscosity of sludge is much higher than that of water. The high viscosity can easily disperse stirring effects within a limited zone around the stirrer, and therefore, lead to poor mixing and insufficient coagulation. Hence, a suitable stirrer design is required, which aims at providing a low and evenly distributed velocity gradient. A low velocity gradient leads to a high mean particle diameter (Kusters 1991). Hence, high velocity gradients should be prevented. Because a high stirrer rotation speed leads to a high-velocity gradient, the stirrer rotation speed was set to be 30 rpm. At a stirrer rotation speed below 30 rpm, sludge particles settled down in the reactor and was, therefore, not used.

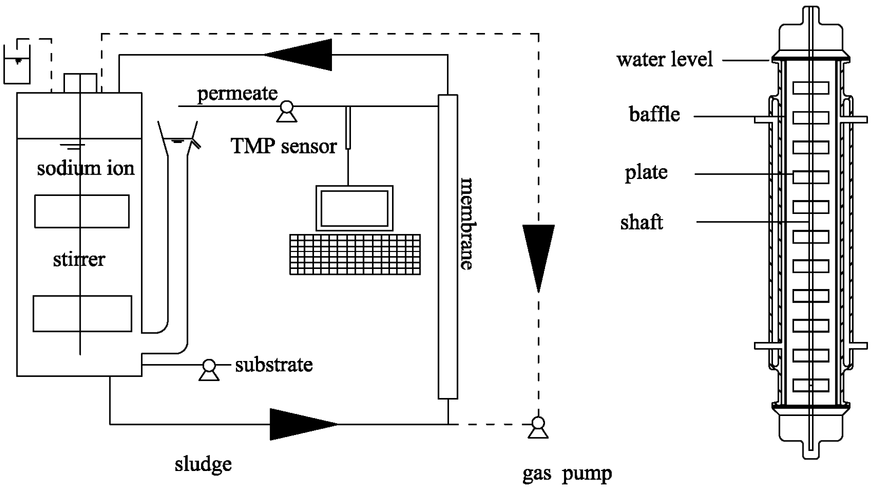

Figure 6.1 Schematic view of the overall setup (left) detailed reactor structure (right)

6.3 Results and discussions

A filtration experiment was done to test whether the hydraulic conditions in the reactor and membrane tube in combination with high salinities could reduce membrane fouling. The TMP as a function of time is depicted in Figure 6.2. Under the applied shear conditions, TMP gradually increased to 29 mbar in 37 hours, while the non-saline sludge was used. Through the external addition of sodium chloride, the salinity of the non-saline sludge was increased from 0 to 10 g/L and then to 20 g/L. The increasing salinity of the non-saline sludge provided an increasing filterability as shown in Figure 6.2. Apparently, the shear conditions were able to provide adequate mixing for coagulation, resulting in a good sludge filterability. Reid et al. (2006) observed that in a short term experiment in aerobic membrane bioreactors, low salt concentrations of 4 g/L negatively impacted the membrane permeability. Similar findings were recently observed by Krzeminski (2013).

Surprisingly, when the saline sludge was used as a filtration bulk solution, the TMP increased sharply from 0 mbar to 200 mbar within 10 hours. The quick TMP increasing rate indicates that saline sludge had a much worse filterability compared to the non-saline sludge and that the applied plug flow regime could not control membrane fouling.

At the start of the experiment it was hypothesized that sodium ions already present in saline wastewaters could be used to induce coagulation for sludge filterability enhancement. However, as shown in Figure 6.2, the applied shear conditions in the reactor apparently did not provide a saline sludge with a good filterability by making use of the large quantities of sodium.

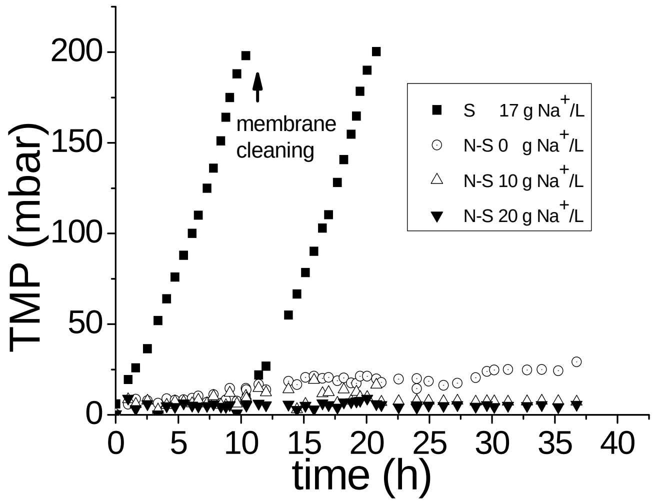

Figure 6.2 TMP over time at a flux of 15 L/m^2.h. S: saline sludge. N-S: non-saline sludge

While the saline sludge was filtrated, serious membrane fouling occurred, despite the applied gas-liquid slug flow that may effectively control membrane fouling (Cui et al. 2003), and the applied low velocity gradient in the mixing chamber that was supposed to induce coagulation. The poor filterability of saline sludge and the inadequacy of Na^+ to induce coagulation in existing saline conditions are further discussed in the below sections.

Firstly and apparently, sodium ions, even present in very high concentration, did not act as a strong coagulant for the saline sludge, while the salinity of the saline sludge was not changed. The applied sodium concentration of 17 g/L in the sludge indeed coagulated fine particles in the saline sludge and made them bigger, which is shown in Figure 6.3a. At the applied velocity gradient, the size of detected biggest particle kept increasing, which indicates that the velocity gradient could promote coagulation. However, the coagulation process did not complete within 30 minutes and possibly a longer time was required (see Figure 6.3a), which indicates that the high salinity of the saline sludge could not contribute to a quick coagulation process. Moreover, the formed aggregates are likely very weak, resulting in small particles release when subjected to a high shear force. In contrast, effective coagulation of fine particles was observed in the non-saline sludge with increasing Na^+ concentrations. The coagulation process was completed within 10 minutes, as indicated in Figure 3b. Similar results were obtained when a higher sodium concentration (20 g/L) was applied. We did not observe a coagulation process in the non-saline sludge when no external sodium was added to the non-saline sludge.

As explained in the Materials and Methods section, the surface charge decreases in the non-saline sludge as its salinity increases, which likely was responsible for the quick coagulation process in the non-saline sludge. Although the measurement of the surface charge of the saline sludge is not possible, it is suspected that the surface charge of this sludge is much higher than that of the non-saline sludge at the same salinity, which led to the slow coagulation process in the saline sludge.

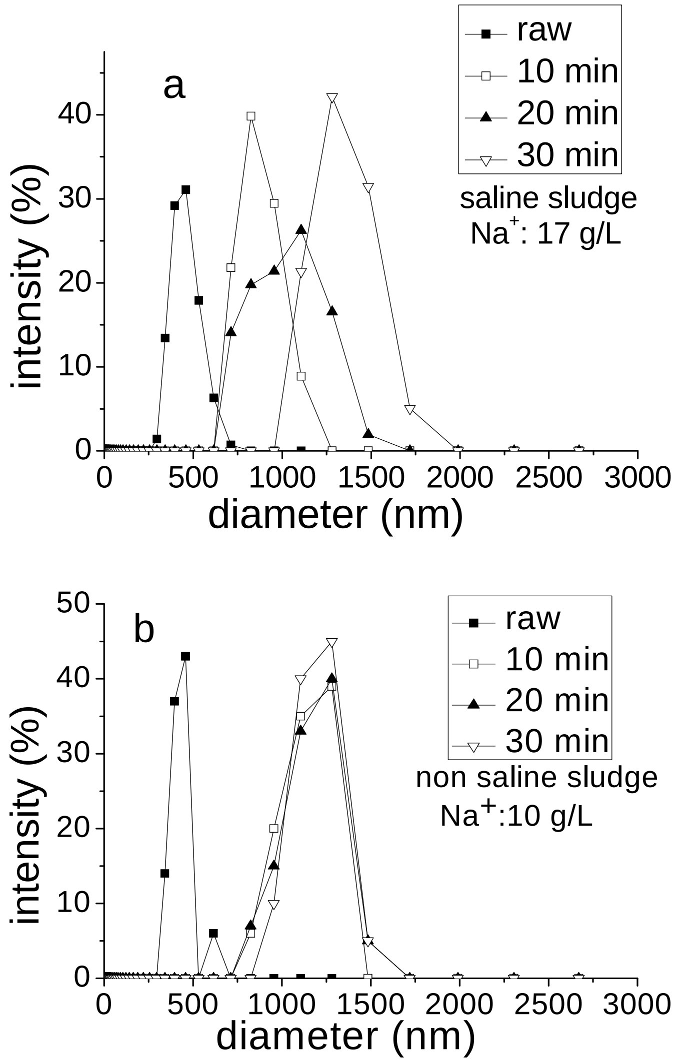

Figure 6.3 Shear induced coagulation of sludge. a) saline sludge with high salinity; b) non-saline sludge with external sodium addition

Although increasing the salinity level of either non-saline or saline sludge might increase the sludge filterability, as was shown for the non-saline sludge, it obviously makes no sense to increase the reactor salinity level in practice. In addition to a possible loss of sludge activity (Lay et al. 2010), the increase in salinity would hamper the discharge of saline effluent to sewerage or the environment, owing to regulations and restrictions.

The poor filterability of saline sludge can secondly be ascribed to formation of a dense cake or gel layer. The cake layer that formed on the membrane surface mainly consisted of carbohydrate and polysaccharide or polysaccharide-like substances that are negatively charged (Fig. 6.6), which is in accordance with reported findings when non-saline sludge is cultured in MBRs (Meng et al. 2009). The existence of negatively charged compounds provided a chance for positively charged ions, i.e. Na^+, to interact with these compounds, to form a compact gel layer (Meng et al. 2009).

In order to study cake layer formation under saline conditions, an experiment was conducted aiming at fouling a membrane intentionally. In order to prevent serious pore blocking by using a high flux, during this period, the flux was kept at a relatively low level of 8 L/m^2.h. This low flux was chosen because a higher flux, such as 15 L/m^2.h, would have been accompanied by much higher TMP increasing rate, as was observed within the shorter term experiments (see Figure 6.2). The TMP developing trend is shown in Figure 6.4. The TMP was low during the first two days. Two plateaus could be observed within the initial four days. However, the TMP increasing rate accelerated later. TMP increased sharply before it reached 200 mbar. The sharp TMP increase indicates that a dense cake layer completely covered the membrane surface, which was confirmed by SEM analysis.

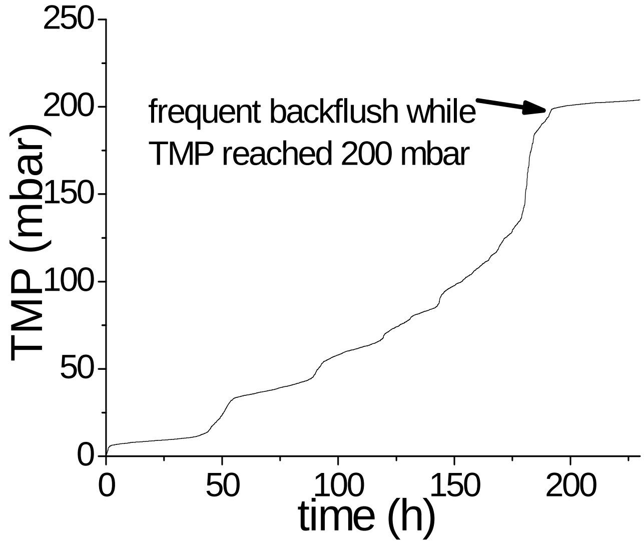

Figure 6.4 Long term TMP profile (saline sludge, 8 L/m^2.h)

Pictures of a new and a fouled membrane are shown in Figure 6.5. At a resolution of 200 μm, the surface of the new membrane was very smooth. After 10 days of operation, the new, originally clean, membrane was completely covered by a dense cake layer, resulting in a high TMP. The frequently applied hydraulic back flush could not effectively maintain TMP at low values. The dense cake layer developed despite the applied two-phase flow and regular back flush. Subsequently, the cake layer was harvested and analyzed for its chemical composition.

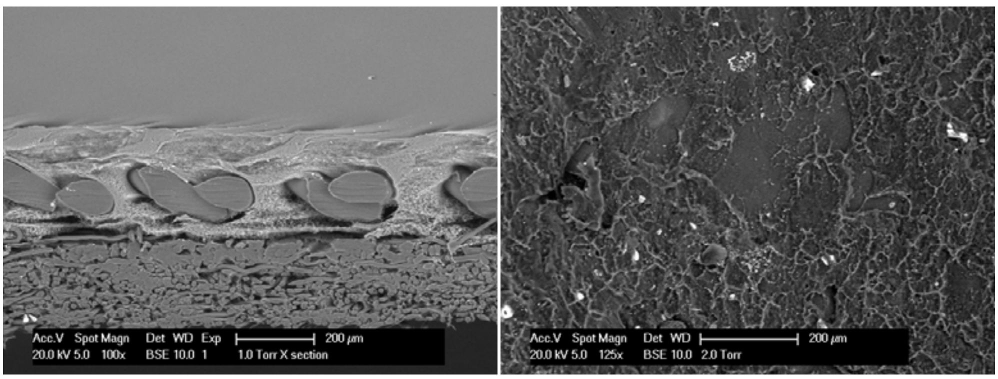

Figure 6.5 SEM analysis of membrane surface
Left: new membrane, side view; right: fouled membrane, top view

The cake layer on the membrane surface was analyzed by an FTIR analysis (Figure 6.6). Distinct aliphatic methylene bands were observed at 2920 and 2850 cm^{-1}, and 1540 cm^{-1} bands can be assigned to microbial biomass (Smidt and Parravicini 2009). Besides, it is known that peaks near 1540 cm^{-1} are indicative for a carbohydrate character (Kim and Jang 2006). The wave number (1420 cm^{-1}) corresponds to strong carbonate band (Smidt and Parravicini 2009). In addition, the broad peak at 1026 cm^{-1} is due to C-O bonds associated with polysaccharide or polysaccharide-like substances (Kimura et al. 2005, Lin et al. 2009).

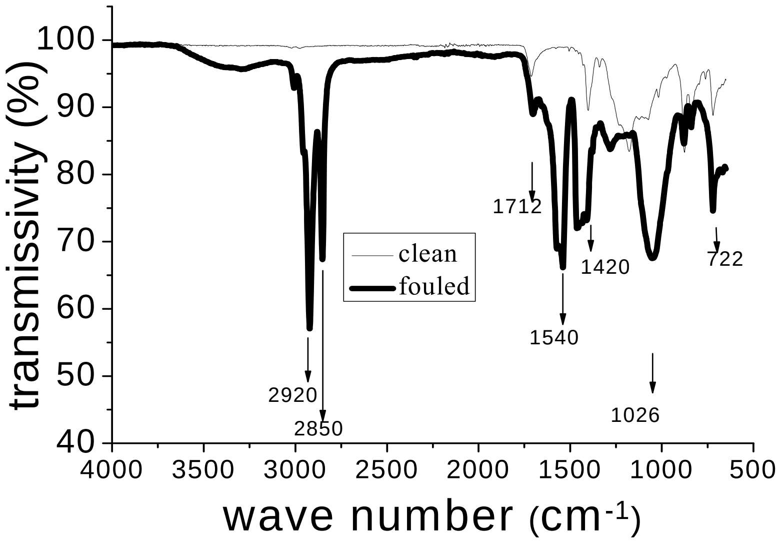

Figure 6.6 FTIR analysis: Wave numbers detected in a sample of the cake layer on the membrane surface

The saline sludge comprised bacteria that are long-term adapted to saline conditions. According to the FTIR analysis, the cake layer that was formed by the saline sludge mainly contained carbohydrate and polysaccharide or polysaccharide-like substances, characterized by negatively-charged functional groups. Positively charged sodium ions may interact with these negatively charged functional groups at membrane surfaces and in cake layers, forming a compact gel layer that promotes the reduction of cake layer porosity layers (Meng et al. 2009).

6.4 Conclusions

In the bioreactor with optimally designed multi-blade mixing, the applied low shear conditions could not promote significant coagulation in the sludge despite its high salinity. Due to the poor coagulation, membrane fouling reduction was not achieved by the application of the low shear conditions.

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Chapter 7

Improving feasibility of saline wastewater treatment by anaerobic membrane bioreactor

Chapter 7 Improving feasibility of saline wastewater treatment by anaerobic membrane bioreactor

Abstract

Chapter 5 and 6 show that, though sodium ions could induce coagulation in saline waters, the shear induced coagulation was weak and therefore could not be used to control membrane fouling. Therefore, a stronger coagulant should be applied to increase sludge filterability. The improvement of the feasibility of saline wastewater treatment by applying anaerobic membrane bioreactors (AnMBRs) was investigated with focus on controlling membrane fouling and increasing sludge activity. As to membrane fouling control, aluminum hydroxyl chloride coagulant was added into an AnMBR. A tubular membrane AnMBR was operated in a side-stream gas-lift mode, while gas and sludge velocities in the membrane were 0.7 and 0.3 m/s, respectively. Salt adapted sludge was cultured in the bioreactor with sodium concentrations in the bulk solution as high as 13 g Na^+/L. The total suspended solids concentration in the reactor was 40 g/L. Results show that a coagulant dose of 0.72 g Al/L could significantly improve membrane flux from 10 to 50 L/m^2.h. The addition of coagulant only slightly decreased sludge activity, whereas average sludge particle size increased and the coagulant was detected on sludge particle surface. Based on these results, coagulant dosing could be considered as a potential way to control membrane fouling under the researched conditions. Furthermore, the saline sludge SMA was increased from 0.4 ± 0.03 g COD CH_4/g VSS.d, to 0.7 ± 0.04 g COD CH_4/g VSS.d, by using chemical additives. Among tested chemicals, the compatible solute glycine betaine and Ni^{2+} increased saline sludge SMA by almost 100 %, whereas K^+, Fe^{2+}, Co^{2+} either showed a less significant effect or had no effect on sludge SMA using the applied dose.

7.1 Introduction

The granulation of anaerobic sludge is problematic under high salinity conditions. Anaerobic granule strength drops significantly, when granules are under long-term exposure to high Na^+ concentrations (Ismail et al. 2008). As a result, the decrease in granule strength can reduce reactors' capacity of sludge retention, which in consequence can cause biomass washout. Ismail et al. (2008) demonstrated that the washed out sludge is characterized by a considerable SMA on acetate, propionate and hydrogen as the substrate. By effectively retaining the washed out sludge inside the reactor, effluent sludge solids concentration would be significantly reduced, while sludge activity is maintained in the reactor. Membrane supported biomass retention using anaerobic membrane bioreactors effectively retains all particles in the reactor. In fact, Vyrides and Stuckey (2009b) and Dereli et al. (2012) already state that AnMBR technology is more suitable to treat saline wastewater than conventional anaerobic reactors.

Sludge methanogenic activity can be severely limited by sodium acting as a non-competitive inhibitor (Speece 1996). In addition to long adaption periods (Ismail et al., 2008), the low sludge SMA caused by sodium toxicity can be increased by adding certain chemicals to the sludge. Compatible solutes and potassium ions are chemicals that can accumulate inside the cell, counteracting sodium toxicity and therefore increase sludge SMA (Vyrides and Stuckey 2009a, Yerkes et al. 1997). Glycine betaine was found to be the most effective compatible solute in terms of increasing sludge SMA (Vyrides and Stuckey 2009a, Yerkes et al. 1997). In addition, trace metals, such as Fe^{2+}, Co^{2+}, Ni^{2+}, also increase sludge SMA when trace metal shortage is apparent (Speece 1996). However, thus far, the impact of saline conditions on trace metal availability is still unknown, nor it is known to what extent saline sludge SMA can be increased by additional trace metals at specific sodium concentrations.

Generally, AnMBRs are limited by relatively low membrane fluxes, worsening their performance efficiency even further when methanogenic activities are limited by high salinity. Reported fluxes of AnMBRs are about 10 $L/m^2.h$ (Jeison et al. 2009a, Jeison et al. 2009b, Torres et al. 2011), which is generally much lower than those obtained in aerobic MBRs (Remy et al. 2009).

Increasing shear stress near the membrane surface is a useful way to improve the membrane flux. However, the increase in shear stress may break anaerobic sludge particles, which may consequently lead to reduced bioreactor biological conversion efficiencies (Brockmann and Seyfried 1996, Stroot et al. 2001) and an increased cake layer resistance and thus decreased operational flux (Jeison et al. 2009b). Conversely, increasing the size of particles that are supposed to be a potential foulant may reduce membrane fouling and thus the shear stress required for achieving high flux (Jeison et al. 2009b).

The use of coagulants in membrane bioreactors can significantly decrease the number of very small particle sizes and subsequently improve membrane flux. Fan et al. (2008) showed that coagulant addition significantly change properties of secondary clarifier effluent and consequently reduces membrane fouling in a post treatment step. Ngo and Guo (2009) directly added coagulants to an aerobic MBR and observed an improved sludge filterability. Koseoglu et al. (2008) tested several types of flocculants and coagulants, i.e. 3 cationic polymers, a biopolymer, a starch, 2 metal salts, and found that the used coagulant can improve critical flux from 37 $L/m^2.h$ to about 54 $L/m^2.h$. Similar research demonstrated that the addition of a coagulant increased the critical flux from 20 $L/m^2.h$ to 30 $L/m^2.h$ (Zhang et al. 2010). Hence, in general, positive effects of dosing coagulants on membrane flux are found but the extent of flux improvement varies, which may relate to many factors such as the type of coagulant used and reactor operation conditions. However, Barbot et al. (2008) showed that not all coagulants give a desirable effect in terms of membrane flux enhancement. Furthermore, it was observed that in aerobic sludge the addition of coagulants reduced the ammonium oxidation efficiency in a short term experiment (Guo et al. 2010), which arises a concern about the potential negative impact of coagulants on sludge activity.

Considering the significant effect of coagulant dosing in aerobic MBRs on membrane fouling control, it is surprising that quite limited research regarding coagulant use in AnMBR has been reported. One study shows that in a fluidized bed - AnMBR, flux could be increased from 15 to 30 $L/m^2.h$ by dosing a coagulant in a short term experiment (Xing et al. 2010). Wu et al. (2009) reported that coagulants can increase the filterability of upflow anaerobic sludge blanket (UASB) reactor effluent but overdose of the coagulant can accelerate membrane fouling tendency. Al-Malack et al. (1996) also showed the positive role of coagulants in reducing membrane fouling in an anaerobic system.

In order to increase the feasibility of saline wastewater treatment by AnMBR, this study focused on increasing saline sludge SMA and reducing membrane fouling at a high sodium concentrations. Selected chemicals, i.e. glycine betaine, K^+, Fe^{2+}, Co^{2+}, Ni^{2+}, were added into the saline sludge inoculum during activity measurements to test whether and to what extent they could increase sludge SMA at the prevailing sodium concentration of 13 g/L. In addition, an aluminum based coagulant was added into an AnMBR in which an adequate shear condition was maintained. The effect of coagulant addition on the filterability of anaerobic sludge was tested, in order to find an optimum dose that could effectively increase membrane flux at the applied shear condition.

7.2 Methods and materials

Reactor operation

Saline sludge was cultured in an AnMBR. A schematic view of the setup and the operation of the AnMBR can refer to chapter 6.

Analysis

PSD was measured by a particle counter (Model 3000, Pacific Scientific Instruments) 30 minutes after the application of the coagulant at each dosage. The particle counter can detect the number of particles with diameters from 2 to 400 µm. Ion concentration at sludge particles' surface was measured by Energy-dispersive X-ray spectroscopy (EDX, Philips XL30). The coagulant used was aluminum hydroxyl chloride (Pluspac Fd Ach, Feralco). The measurement of the number of submicron particles can refer to chapter 3. Each measurement was repeated twice and data were obtained while detected particle numbers were stable.

SMA

SMA test was performed in an Automatic Methane Potential Test System (Bioprocess Control, Sweden). During the SMA tests, acetate (initial concentration 2.2 g COD/L) was used as the substrate and sludge concentration was 4.0 g/L. Salinity was adjusted accordingly by the addition of NaCl. The total volume of the mixture of sludge and medium was 400 ml. The chemical additives in the SMA tests included glycine betaine, K^+, Fe^{2+}, Co^{2+} and Ni^{2+}. Different dosages of each chemical were applied and the SMAs at all dosages of a specific chemical were measured at the same time.

7.3 Results and discussion

7.3.1 Effect of dosing coagulant on membrane fouling

As can be seen in Figure 7.1, frequent hydraulic back flush was required to recover low TMP values even when the flux was as low as 10 L/m^2.h. In addition, the back flush could not completely prevent TMP from increasing, since an overall slowly TMP increasing trend still could be observed. The apparent TMP increasing rate at the low flux indicates that the filterability of the anaerobic sludge was bad, which was generally observed in previous investigations (Jeison et al. 2009b).

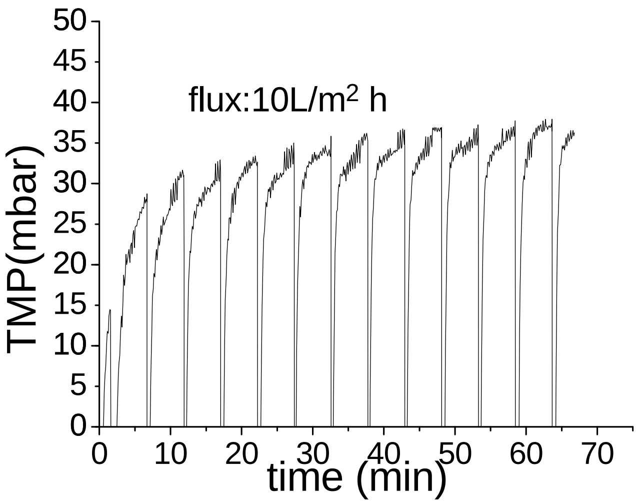

Figure 7.1 TMP variation under backwash regime without coagulant addition

To improve the filterability of the sludge, aluminum hydroxyl chloride was added into the reactor. Figure 7.2(a) shows that a low dose of coagulant (0.48 g Al /L) effectively restrained the increase in TMP at a relatively high flux (15 L/m^2.h). The TMP was maintained around zero mbar in comparison with 30 mbar when the flux was 10 L/m^2.h and no coagulant was added. When an even higher flux was applied (30 L/m^2.h), only a small increasing trend was observed within 10 minutes. However, the TMP rose to 120 mbar within 70 hours, even if intermittent back flush was applied, as shown in Figure 7.2(b) (TMP during back flush is not shown). Therefore, although aluminum hydroxyl chloride could be used to improve filterability of anaerobic sludge, it was not possible to achieve a very high flux with low or no TMP increase.

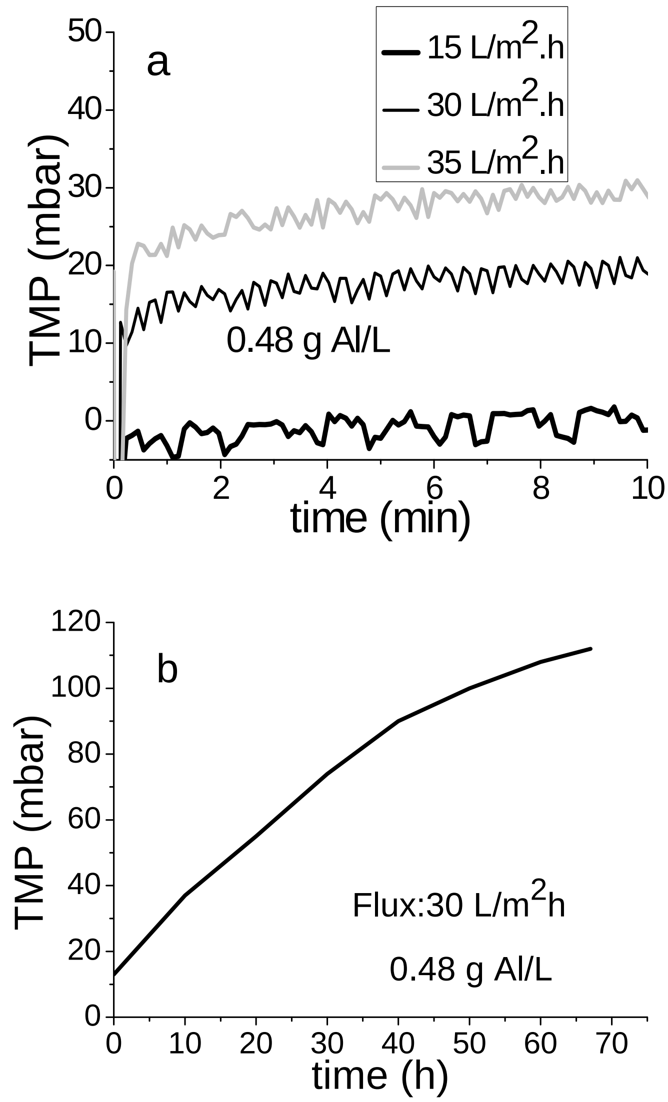

Figure 7.2 TMP variation after coagulant addition (0.48 g Al /L) on the short term for various fluxes (a) and the long term for fixed flux (b)

Hereafter, more coagulant was added to reach a dosage up to 0.72 g Al/L. By this further addition, the membrane filtration performance was significantly improved. Figure 7.3(a) shows that, during a period of several hours, the TMP did not increase at all, even when the flux was as high as 50 L/m^2.h. Compared to the low filterability of anaerobic sludge and even worse filterability under saline conditions as reported by others (Akram and Stuckey 2008, Tam et al. 2006), aluminum hydroxyl chloride addition allowed achieving a very high short-term flux. Subsequently, higher fluxes were applied at the same dose. The TMP as a function of time at various fluxes is depicted in Figure 7.3(b). When the fluxes were lower than 70 L/m^2.h, the TMP increasing rates were small but a low increasing trend could be observed. An even higher coagulant dose was also tested (0.96 g Al/L), however, no further improvement of membrane flux was found.

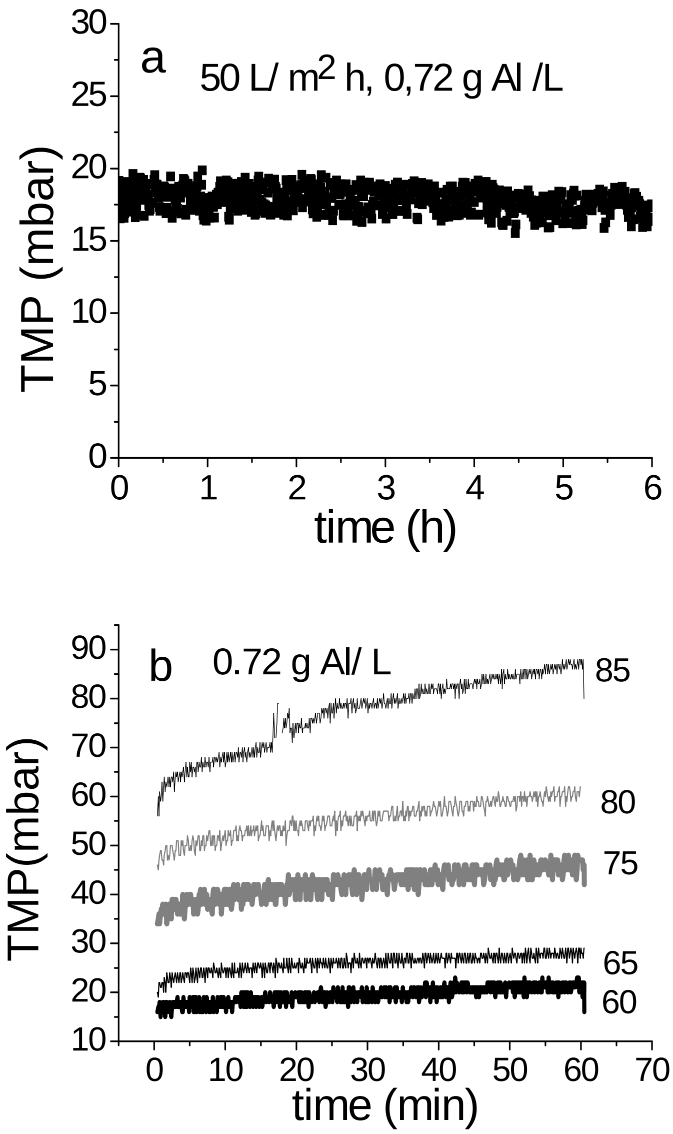

Figure 7.3 TMP at coagulant dose of 0.72 g Al/L. a: fixed flux; b: various applied fluxes (in L/m^2.h)

7.3.2 Effect of dosing coagulant on PSD and sludge activity

Sludge particle size plays two roles in anaerobic membrane bioreactors, i.e. related to membrane fouling and to biomass activity.

Membrane fouling occurs when particles accumulate at the membrane surface owing to the drag force induced by the membrane permeation flux (Choo and Lee 1998). Fouling control includes back transport of potential foulants to the bulk liquid by applying a shear force. There are three forces that govern the back transport of particles from the membrane surface to a bulk solution, i.e. inertial lift, shear-induced diffusion and Brownian diffusion. Small particles are difficult to be back transported to a bulk solution, compared to a big particle.

Anaerobic flocs and aggregates are bigger than dispersed sludge, which indicates that sludge aggregation could be useful to reduce membrane fouling and/or increase membrane flux. Among many theories that try to explain the formation of anaerobic conglomerates, eventually evolving in granular sludge, the selective wash out of dispersed sludge is regarded crucial (Hulshoff Pol et al. 2004). However, there is no selection pressure in AnMBRs as all sludge is retained by a membrane and, therefore, sludge granulation cannot be expected. Nonetheless, big particles can be formed by using coagulants that can effectively (cross) link very small particles to large aggregates. Another advantage of sludge aggregation is enhancing robustness of the anaerobic reactor system, being less susceptible for changes in temperature, toxicant concentrations and loading rates. The latter can be explained by the occurrence of mass-transfer limited catabolic conversions in (granular) aggregates. Additionally, the juxta-positioning of syntrophic species in such aggregates ensures efficient conversion of complex compounds in which interspecies hydrogen transfer is involved (Stams and Plugge 2009). Thus far, it is not clear how and to what extend the addition of coagulants can influence sludge aggregation and concomitantly impact the sludge SMA.

Effect on particle size

The added coagulant did not significantly increase particle sizes between 2 and 10 µm, as is shown in Figure 7.4. However, a dose of 0.48 g Al/L aluminum apparently combined small particles and formed larger particles as a reduced number of small particles was observed. A dose of 0.72 g Al/L further enhanced this effect. However, the highest aluminum dose (0.96 g Al/L) did not cause a further improvement.

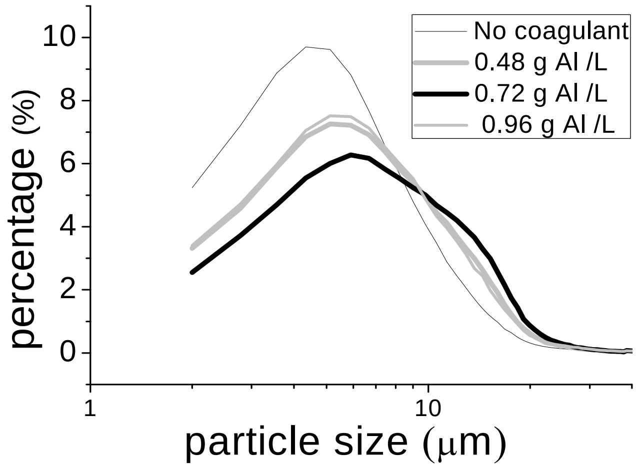

Figure 7.4 PSD in the bioreactor at various doses of coagulant (number based percentage)

By comparing the significant improvement in sludge filterability and notable but limited reduction in the number of particles < 5 µm, we conclude that particle sizes between 2 and 10 µm did not play an important role in determining filterability of anaerobic sludge. In this respect, it must be noted that addition of 0.96 g Al/L gave higher membrane fluxes than in the case of 0.48 g Al/L, while particle sizes distribution between 2 and 10 µm were very similar.

Effect on sludge activity

The activity of biomass in the reactor should be maintained while the coagulant is added. In wastewater treatment, some authors postulate that the addition of a cationic coagulant promotes the formation of anaerobic granular sludge (Wang et al. 2004). However, big particles with an increased particle size, which results from the addition of coagulants in an AnMBR, may act differently than the self-aggregated methanogenic conglomerates. Therefore, it is not clear if and to what extent the addition of a coagulant impacts the sludge SMA. Based on EDX analysis (Table 1), it can be concluded that a fraction of the aluminum was attached to the sludge particle surface.

Table 7.1 Ion concentrations on particle surface (Atom percentage, %)

	Na^{+}	Mg^{2+}	Ca^{2+}	Al^{3+}	Fe^{3+}
0 g Al/L	30.61	0.11	5.15	0.36	1.83
0.96 g Al/L	17.02	0.51	1.06	6.29	2.26

When no coagulant was added, the sludge activity was about 0.4 g COD CH_4/g VSS.d. The addition of the coagulant only slightly decreased the sludge activity from 0.39 g COD CH_4/g VSS.d to 0.38 and 0.37 g COD CH_4/g VSS.d at 0.72 g Al/L and 0.96 g Al/L, respectively. The standard deviations for these SMA measurements were 0.03 g COD CH_4/gVSS.d Considering its negligible effect on sludge SMA and considerable improvement of sludge filterability, dosing of aluminum coagulant has a clear potential to improve the efficiency of AnMBRs.

7.3.3 Long term TMP development

Figure 7.5 shows that, although a low TMP was observed at the beginning of the long term experiment, it gradually rose afterwards. However, the time for reaching a similar high TMP as for sludge without coagulant was greatly extended when the coagulant was added.

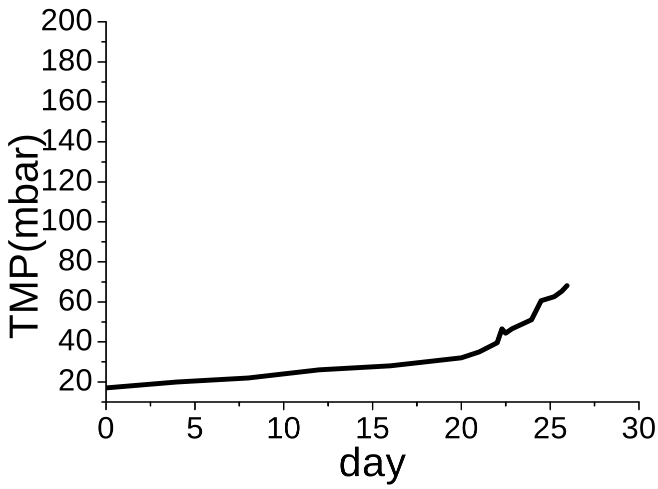

Figure 7.5 Long term TMP development (50 L/m^2.h, 0.96 g Al/L)

The TMP more drastically rose during days 20 and 30 of the AnMBR operation days, possibly caused by accumulation of sub-micron particles, which can be explained by the decrease in sludge filterability due to the increase in the number of sub-micron particles in the reactor. The latter, also referred to as colloids, are regarded as a major membrane foulant (Meng et al. 2009). The addition of the coagulant significantly decreased the number of the submicron particles from 2.5×10^5 to 1.7×10^5 particles per liter within one day, which contributed to the observed increase in sludge filterability in the short term experiment. However, after 30 days of continuous operation the particle number increased to almost its initial value: 2.3×10^5 per liter.

It is argued that the increase in the number of sub-micron particles in the long term experiment was mainly due to the breakage of the flocs formed by the coagulant. It is hypothesized that by adding the coagulant, sub-micron particles are scavenged resulting in increased sludge filterability. However, on the more long term, the coagulant-based large flocs broke into smaller (sub-micron) particles due to shear stress in the reactor, e.g. in the tubular membrane. In addition, it is reported that the coagulation capacity of coagulants keeps decreasing even when the concentration of coagulants is constant (Li et al. 2007, Yukselen and Gregory 2004a, b). Obviously, during long-term operation sub-micron particles are also continuously produced, resulting from substrate conversion and other bioactivities. Therefore, we expect that the number of sub-micron particles gradually increases in continuous operation, resulting in a gradual deterioration of the sludge filterability. As a consequence, periodic coagulant dosage is regarded imperative to ensure stable AnMBR operation at high flux and low TMP. Such periodic coagulant dosage requires an advanced control strategy that aims at effective membrane fouling reduction as well as preventing an unlimited rise of the coagulant concentration in AnMBRs. Further optimization studies in this are required.

7.3.4 Factors influencing sludge activity

High salinity impacts sludge SMA. The effect of the sodium concentration on the SMA of our reactor sludge is shown in Figure 7.6, indicating a maximum SMA at 13 g Na^+/L.

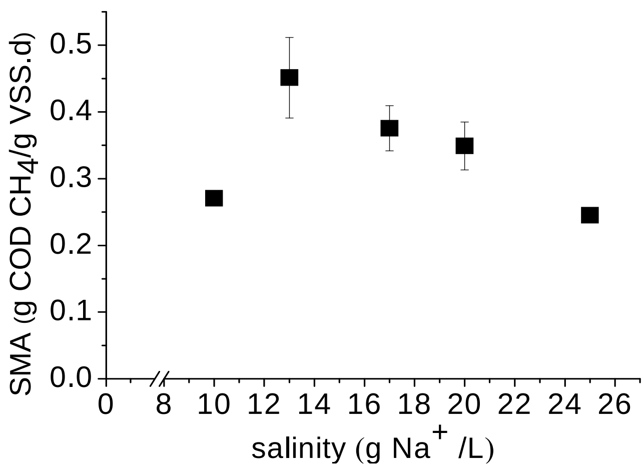

Figure 7.6 Effect of Salinity on specific methanogenic activity

As expected, sludge activity gradually decreased, when the sodium concentration increased from 13 g/L to 25 g/L. However, and very strikingly, a decrease in Na^+ concentration by 3 g/L to 10 g Na^+/L caused a much lower SMA compared to the SMA with a Na^+ increase by 3 g/L. Apparently, the decrease in salinity had a more profound impact on microorganism activity than an equal increase in salinity, which is in accordance with findings reported by others (Ventosa 2004). As shown in Figure 7.6, the SMAs were lower than the typical SMA values of granular sludge grown in industrial anaerobic reactor systems, i.e. 0.5-1.0 g COD CH_4/g VSS.d (van Lier et al. 2008).

To study the potentials of selected chemicals for improving biomass SMA under saline conditions, SMA was measured as a function of increasing concentrations of glycine-betaine and potassium. The results of the impact of selected chemicals on SMA are shown in Figure 7.7 and 7.8. When the concentration of glycine-betaine increased from 0 to 20 mmol/L, the SMA increased from 0.5 to 1 g COD CH_4/g VSS.d. The doubling of SMA indicates that the glycine-betaine may be used to effectively increase the sludge activity and thereby facilitate higher organic loads of reactors (Vyrides and Stuckey 2009a).

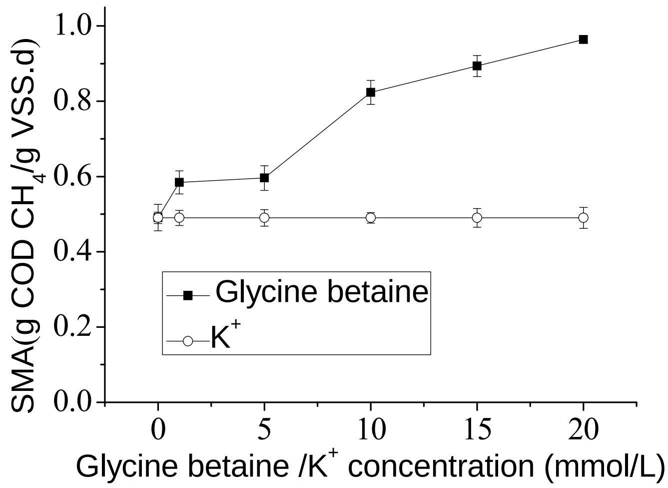

Figure 7.7 Effect of the addition of glycine betaine and K^+ on SMA (sodium: 13 g/L)

In order to combat osmotic pressure difference across cell walls, compatible solutes are synthesized by microorganisms. However, in any case, uptake of external compatible solutes from the medium is preferred over the synthesis de novo (Ventosa et al. 1998). Besides the addition of glycine betaine, the effect of the addition of potassium ions on SMA of the saline sludge was also tested. However, no SMA increase was observed even when the potassium ion concentration was up to 30 mmol/L. It has been shown that potassium ions are remarkably effective for colonizing of habitats with permanent high salinities (Ismail et al. 2012), but is far less useful in coping with habitats of increased salinity (20-80 g Na^+/L) (Ventosa et al. 1998).

Under high salinity conditions, trace metal requirements may differ unexpectedly. It is known that the functionality of essential methanogenic co-enzymes, such as F430, is highly dependent on the presence of heavy metals, i.e. Ni^{2+}. Figure 7.8 shows that Fe^{2+} and Ni^{2+} increased the activity of the saline sludge by 48 % and 97%, respectively. We observed that doses below the applied concentrations of 300 µmol/L for Fe^{2+} and 30 µmol/L for Ni^{2+}, did not provide any effect on the activity (data not shown). Therefore, it appears that the two concentrations are in the range of the minimum requirements to enable the methanogens to function well under the saline conditions. Apparently, there exists a threshold dosage for the SMA stimulatory effect of Fe^{2+} and Ni^{2+}. Other results show that the addition of Co^{2+} with concentrations up to 30 µmol/L did not increase the SMA.

From our research we postulate that chemical additives such as compatible solutes and heavy metals stimulate bacterial catabolic activities and likely also its growth under saline anaerobic conditions. The increase in sludge production rates would allow more frequent sludge discharges, opening perspectives for coagulant refreshment and thus membrane flux enhancement.

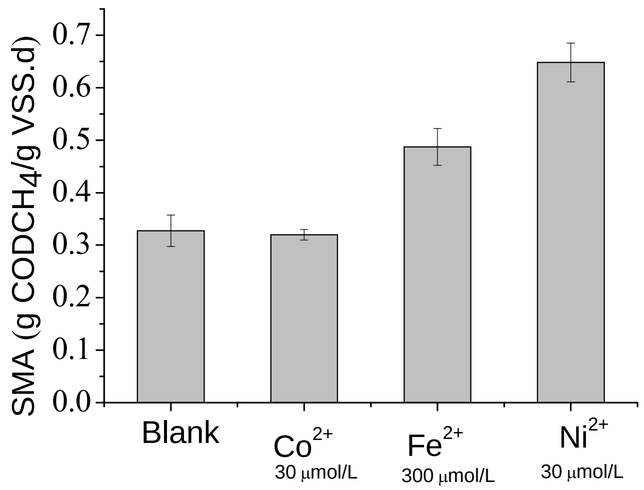

Figure 7.8 Effect of trace metals on SMA (sodium: 13 g/L)

7.4 Conclusions

Dosage of aluminum hydroxyl chloride coagulant did effectively improve the filterability of anaerobic sludge, which enabled a significant short-term increase in membrane flux. In addition, sludge activity was hardly influenced by the coagulant. However, long-term flux enhancement could not be sustained. The saline sludge SMA could be increased from 0.2-0.5 g COD CH_4/g VSS.d to up to 1.0 g COD CH_4/g VSS.d by adding selected chemicals. Glycine-betaine and Ni^{2+} did significantly enhance the SMA, whereas K^+, Fe^{2+}, Co^{2+} either showed less significance or had no effect on sludge activity.

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Chapter 8

General discussion and summary

Chapter 8 General discussion and summary

8.1 Problem definition and the scope of the thesis

Anaerobic granular-based bioprocesses are known to be highly efficient, but anaerobic sludge granulation cannot be guaranteed while treating specific types of wastewaters under more extreme conditions, such as high temperatures, high salinity, fluctuating loading conditions, etc. For instance, granulation under saline conditions proceeds much more difficult because salt can induce the disintegration of flocs and granules (Pevere et al. 2007). Poor granulation in sludge bed systems appears to result in reduced sludge retention, potentially affecting reactor efficiencies. Where sludge granulation cannot proceed successfully, low reactor efficiencies can therefore be expected, revealing the need for a technique that can effectively retain sludge particles within reactors. Combining membranes with anaerobic reactor technology into what is known as an anaerobic membrane bioreactor (AnMBR), allows high sludge concentrations independent of sludge settleability. However, a problem with AnMBRs is that generally observed membrane fluxes are about 10 L/m^2.h, which is regarded as low. Particularly for the more diluted waste streams the mentioned flux needs to be effectively increased. This thesis is therefore directed towards developing measures enabling AnMBR operation at high membrane fluxes, doubling or tripling the current flux limits. Saline wastewater was selected as the main example to be used in these investigations.

Large quantities of saline wastewater are discharged every year. The sodium ions in these saline wastewaters can have a negative impact on biological wastewater treatment efficiency. In addition, retention of biomass is difficult when highly saline wastewaters are treated by means of high-rate anaerobic bioprocesses. Nevertheless, an AnMBR provides an effective way to retain sludge particles in reactors, allowing high solid retention times (SRTs). Therefore, an AnMBR would be expected to treat highly saline wastewaters more efficiently than conventional bioprocesses. In order to assess the potentials of saline wastewater treatment by AnMBR the behaviour of sludge under saline conditions, i.e. the effect of salt on sludge biological and morphological properties and the susceptibility of AnMBR sludge for salinity fluctuations, needs to be investigated.

Membrane fouling is a key issue when applying membrane techniques. The flux rates in AnMBRs are generally much lower than those in aerobic MBRs, which likely can be attributed to the abundant occurrence of single cell organisms under anaerobic conditions (Jeison et al. 2009). Moreover, under aerobic conditions, high dissolved oxygen concentrations stimulate floc formation, enhancing sludge filterability and cake layer porosity, subsequently leading to an increased membrane flux. Increasing the membrane flux in AnMBRs is considered crucial for further developing the technology for a wide range of practical applications. Membrane flux in aerobic MBRs can be effectively increased by adding coagulant or powdered activated carbon (Koseoglu et al. 2008, Remy et al. 2009, 2010). Compared to aerobic MBRs, however, membrane fouling reduction in AnMBRs has received much less attention.

This thesis therefore focuses mainly on developing methodologies to reduce membrane fouling in AnMBRs.

Particles in sludge can be classified on the basis of their size, with the fine particles being potential membrane foulants. Many researchers, however, analyze membrane foulants using physical-chemical methods identifying extracellular polymeric substances (EPSs) as membrane foulants (Meng et al. 2009). Changing the reactor operational parameters can change the physiological status of flocs in reactors, which can in turn have an impact on EPS synthesis and its release into sludge bulk solution. Therefore, many researchers try to reduce membrane fouling by changing reactor operational parameters, e.g. by controlling sludge retention time, hydraulic retention time, organic load, etc. However, such changes obviously restrict the freedom of reactor operation. An attempt has also been made to expand activated sludge modeling by including EPS production (Jiang et al. 2008). While, based on the author's modeling results, it might be possible to control EPS production through managing operation parameters, such as sludge retention time, the expanded model increases the complexity of activated sludge modeling. The actual effectiveness of the expanded activated sludge model in controlling membrane fouling has not been reported.

In the underlying research, fine particles are considered the main potential membrane foulant. More specifically, the research focus was on controlling the presence of submicron-sized particles, i.e. colloids such as EPS, which are widely accepted to be membrane foulants (Meng et al. 2009).

In this thesis, two approaches have been followed, i.e. improving slug flow in tubular membranes, and improving sludge filterability, in order to achieve a high membrane flux. Applying improved slug flow aimed to enhance the shear stress at the membrane surface to move membrane foulants away from the membrane surface. Improving sludge filterability aimed to reduce the number of submicron-sized particles in the sludge liquor. Chapters 2 and 3 show that slug flow can achieve a membrane flux as high as 25 $L/m^2.h$ without any TMP increase over 45 hours, provided that the sludge filterability was much better than a normal suspended sludge filterability that just allows low membrane fluxes, e.g. 10 $L/m^2.h$. Based on these results, chapters 4 to 7 then focus on finding a method that can provide improved sludge filterability. Dosing coagulant was found to be a promising approach for improving sludge filterability. By applying slug flow together with coagulant dosing, an auto-control strategy for membrane fouling reduction could be developed, which is recommended for further studies.

8.2 Shear stress and filterability

In the past, there has been a dilemma concerning conflicting ideas with regard to shear stress and filterability. A high shear stress on a membrane surface has been thought to provide an easy way to remove foulants from the membrane surfaces, and hence to reduce membrane fouling. However, sludge filterability can also be reduced by high shear stress, as it can produce a reduction in particle size, which in turn contributes to membrane fouling (Jeison et al. 2009). Uncertainty has therefore remained over whether or not high shear stress should be applied.

By optimizing the nozzle size, gas velocity, and diameter in the tubular membrane of an AnMBR, optimized shear stresses reaching up to 15 Pa were applied at the membrane surface, using slug flow (chapters 2 and 3). When optimized shear stress was applied, whether or not a high flux of 25 L/m^2.h could be realized depended on the sludge filterability. When applying the shear stress at the membrane surface, the filterability of the sludge was found to have a strong influence on the transmembrane pressure at a steady flux. It was also demonstrated in long term experiments (100 days) that an applied slug flow that generally resulted in a shear stress of about 20 Pa in the bulk sludge solution (Chapter 3), also resulted in a stable particle size distribution.

The above discussion shows that optimized slug flow can result in a high membrane flux of 25 L/m^2.h with almost no increase in TMP, provided that the sludge filterability is improved from the filterability of a conventional suspended sludge. Future research on this topic should therefore focus on how to improve sludge filterability rather than on managing shear stress, thus allowing the shear stress dilemma to be avoided. The remainder of this thesis deals with improving sludge filterability by means of adding adsorbent and coagulant.

8.3 Feasibility of adsorption

It has been demonstrated that the addition of an adsorbent (usually PAC, or zeolite) to aerobic MBRs can help reducing membrane fouling (Meng et al. 2009). The PAC will eventually lose its effectiveness and need to be refreshed, which can be achieved by removing the old PAC from the MBR and adding new PAC. PAC can also help to reduce membrane fouling in an AnMBR (Chapter 4), although the effect was found quite limited under the conditions investigated. In view of the fact that the refreshment of PAC results in sludge loss, and since anaerobic bacteria only grow very slowly, the application of PAC for membrane fouling reduction in AnMBRs must be considered to be of dubious merit.
In order to make use of the positive effect that dosing adsorbents might have in reducing membrane fouling and at the same time prevent sludge loss during adsorbent refreshment, a magnetic adsorbent was synthesized and its effectiveness in reducing membrane fouling was tested (Chapter 4). Surprisingly, experiments showed that the magnetic adsorbent significantly decreased the sludge filterability attributable to the fact that the magnetic adsorbent was colloid-sized. Moreover, its removal still resulted in significant sludge loss. The observed constraints limit the use of magnetic adsorbents.

8.4 Impact of coagulation on membrane fouling

Coagulation can be effective in reducing the quantity of fine particles in solutions and can therefore be used as a pre-treatment method to reduce membrane fouling. Coagulation can also be achieved within reactors, thus reducing the amount of system space required.

An attempt was made to use the sodium ions in saline wastewaters to induce coagulation in an AnMBR (chapters 5 and 6). It was hypothesized that the sodium ions in highly saline wastewaters could possibly be used as a coagulant, which would then avoid the need for any external coagulant. In Chapter 5 the coagulation of fine particles in non-saline sludge is shown to be significantly increased by raising the salinity, suggesting the possibility that the sodium ions in saline wastewater could indeed be used to reduce membrane fouling. However, in Chapter 6 it is demonstrated that, although increasing the salinity in a non-saline sludge helps to reduce membrane fouling, the salinity in saline wastewater does not achieve the same result. Sodium can only act as an effective coagulant, when its introduction is accompanied by a significant change in ionic strength. Simply stirring a sodium-saturated sludge will thus not result in any coagulation. High salinity as such does not therefore contribute significantly to the reduction of membrane fouling in highly saline sludge. In addition, the poor filterability of saline sludge is also ascribed to its low floc strength.

From the research presented in chapters 5 and 6 we conclude that it is not possible to use the sodium ions in saline wastewaters to control membrane fouling. The addition of an external coagulant is therefore necessary to reduce the quantity of fine particles in saline sludge, thereby increasing its filterability. The slug dose addition of an aluminum coagulant was found to effectively increase the sludge filterability (Chapter 7). A long term experiment showed, however, that after such a slug-dose the TMP increased very slowly over a period of one month. It is suggested therefore that aluminum-based coagulants are not very effective for long term fouling control, as they gradually lose their coagulation ability, whereas fine particles continue to be produced and consumed during the bioprocessing. Refreshment of the coagulant is therefore required. The addition of coagulant only slightly decreased sludge activity, whereas the average sludge particle size increased and the coagulant was detected on sludge particle surfaces. Based on these results, coagulant dosing could be considered as a potential method for controlling membrane fouling (under the investigated conditions). Furthermore, the saline sludge specific methanogenic activity (SMA) was increased from 0.40 ± 0.03 g COD CH_4/g VSS.d, to 0.70 ± 0.04 g COD CH_4/g VSS.d, by using chemical additives. Of the chemicals tested, the compatible solute glycine betaine and Ni^{2+} increased saline sludge SMA by almost 100%, while the applied doses of K^+, Fe^{2+}, and Co^{2+} either showed a less significant effect, or had no effect at all on sludge SMA.

8.5 Recommendations for further research

The combination of applying slug flow and adding aluminum coagulant enables membrane operation at a high flux (50 L/m^2.h) and a low TMP (< 80 mbar) over short periods of time, i.e. up to one month. However, the number of fine particles can increase again in long-term experiments, an intelligent coagulant dosing strategy needs to be developed, which should include:

a) Automatic recognition of the optimal time for coagulant refreshment, and the prevention of coagulant accumulation in (An)MBRs. Likely, this can be based on discerning a threshold TMP increase rate or a threshold number of fine particles, followed by coagulant refreshment.

b) Avoidance of frequent coagulant refreshments, since such refreshments result in significant sludge losses. Frequent refreshments can dilute methanogenic bacteria concentrations, which would potentially result in a decrease in both the pH and the reactor efficiency.

8.6 References

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Hoofdstuk **8**

Samenvatting en algemene discussie

Hoofdstuk 8 Samenvatting en algemene discussie

8.1 Probleemdefinitie en doelstellingen

Anaerobe op korrelslib gebaseerde afvalwaterzuiveringsprocessen zijn zeer efficiënt voor de behandeling van industrieel afvalwater (van Lier, 2008). Echter, de groei van anaeroob korrelvormig slib kan niet worden gegarandeerd bij de behandeling van bepaalde typen afvalwaters onder meer extreme condities. Bij deze extreme condities kan worden gedacht aan hoge temperaturen, hoge zoutgehaltes en fluctuerende belasting. Bijvoorbeeld stabiliteit en groei van korrelslib onder zoute condities is veel moeilijker omdat zout desintegratie van vlokken en korrels kan veroorzaken (Pevere et al. 2007). Het uiteenvallen van slibkorrels en/of de afwezigheid van de aanwas van korrelslib in slibbedsystemen leidt in veel gevallen tot een gereduceerde slibretentie, wat de reactorefficiëntie negatief beïnvloedt. Voor de meer extreme afvalwaters waarop groei van korrelvormig slib moeilijk of niet mogelijk is, dient de benodigde hoge slibretentie op een andere wijze te worden verkregen. Het combineren van membranen met anaerobe reactortechnologie, in wat bekend staat als de anaerobe membraanbioreactor (AnMBR), maakt het mogelijk hoge slibconcentraties te bereiken onafhankelijk van de bezinkingsnelheid van het slib. Op basis van tot dusver uitgevoerd onderzoek blijkt echter de haalbare membraanflux in een AnMBR in de orde van 10 $L/m^2.h$ te zijn, wat als te laag wordt beschouwd voor commerciële exploitatie. Vooral voor de meer verdunde afvalwaterstromen moet de flux afdoende worden verhoogd voor het verkrijgen van een competitieve technologie. Dit proefschrift is daarom gericht op het ontwikkelen van strategieën in de bedrijfsvoering om in het AnMBR proces de membraanfluxen significant te kunnen verhogen. Doelstelling is het verdubbelen of zelfs verdrievoudigen van de huidige fluxlimieten. Gezien de industriële interesse is zout afvalwater bij dit onderzoek centraal gesteld.

Jaarlijks worden grote hoeveelheden zout afvalwater geloosd. De natriumionen in dit zoute afvalwater kunnen een negatief effect hebben op het rendement van de biologische zuivering. Enerzijds remt zout de biologische activiteit, anderzijds is de retentie van biomassa problematisch wanneer zeer zout afvalwater wordt behandeld. Bij de toepassing van een AnMBR is effectieve slibretentie echter gegarandeerd, waardoor hoge slibconcentraties en een lange slibretentietijd (SRT) mogelijk is. Naar verwachting maakt een AnMBR een efficiëntere behandelding van zeer zout afvalwater mogelijk. Om de mogelijkheden van zout-afvalwaterbehandeling door AnMBR te beoordelen dient het gedrag van slib onder zoute omstandigheden nader te worden onderzocht, dat wil zeggen: het effect van zout op zowel de biologische en morfologische eigenschappen van slib als de gevoeligheid van AnMBR-slib voor schommelingen in het zoutgehalte. Genoemde morfologische eigenschappen spelen een belangrijke rol in het membraanfiltratieproces en de te verwachten membraanvervuiling.

Huidig onderzoek laat zien dat de membraanfluxen in AnMBRs in het algemeen veel lager zijn dan die van aerobe MBRs. Dit is waarschijnlijk toe te schrijven aan het in overvloed voorkomen van eencellige organismen en andere zeer kleine zwevende-stofdeeltjes onder anaerobe condities (Jeison et al. 2009). Bij aerobe MBRs worden deze kleine deeltjes vaak weggevangen door het aanwezige actiefslib dat onder invloed van hoge concentraties opgeloste zuurstof vlokvorming stimuleert. Vlokvorming verbetert de filtreerbaarheid van het slib en de porositeit van de koeklaag, wat tot een verhoogde membraanflux leidt. Verhoging van de membraanflux in AnMBRs wordt beschouwd als cruciaal voor de verdere ontwikkeling en verbreding van de toepassingsmogelijkheden van deze technologie. In aerobe MBRs kan de membraanflux effectief worden verhoogd door toevoeging van een coagulant of actiefkoolpoeder (PAC) (Koseoglu et al. 2008, Remy et al. 2010, Remy et al. 2009). Dergelijke remediërende maatregels zijn in AnMBR systemen nog niet onderzocht. Dit proefschrift richt zich daarom vooral op de ontwikkeling van methodes om membraanvervuiling in AnMBRs te verminderen en/of effectief te beheersen.

Bij filtratieonderzoek worden de deeltjes in het slib geclassificeerd op basis van hun grootte, waarbij met name de kleine deeltjes verantwoordelijk zijn voor membraanvervuiling en/of verdichting van de filtratie-koeklaag. Naast deeltjesgrootte analyseren veel onderzoekers membraanvervuiling door middel van fysisch-chemische methoden, waarbij extracellulaire polymeersubstanties (EPS) worden aangemerkt als zijnde verantwoordelijk voor de waargenomen membraanvervuiling (Meng et al. 2009). Het veranderen van operationele parameters van de reactor kan de fysiologische status van de vlokken in de reactor veranderen. Deze kunnen op hun beurt invloed hebben op de EPS-synthese en het vrijkomen van het EPS in de slib-bulkoplossing. Diverse auteurs proberen membraanvervuiling te verminderen door het veranderen van de operationele parameters van de reactor, zoals het aanpassen van de slibretentietijd, hydraulische retentietijd, organische belasting, enz. Zulke veranderingen beperken uiteraard wel de vrijheid van de bedrijfsvoering van de reactor wat normaliter in praktijksituaties niet mogelijk is. Verder is er een poging gedaan om simulatiemodellen voor actiefslib uit te breiden met EPS-productie (Jiang et al. 2008). Op basis van deze modeleerresultaten kan inderdaad worden vastgesteld dat de EPS-productie kan worden beïnvloed door operationele parameters zoals slibretentietijd. Echter de uitbreiding verhoogt de complexiteit van het actiefslibmodel. De werkelijke effectiviteit van het uitgebreide actiefslibmodel in het beheersen van de membraanvervuiling is niet gerapporteerd en is derhalve niet verder meegenomen in dit promotieonderzoek.

In het onderhavige onderzoek worden kleine deeltjes beschouwd als de belangrijkste potentiële membraanvervuilers. Meer specifiek heeft het onderzoek zich gericht op het beheersen van de aanwezigheid van sub-micron deeltjes dat wil zeggen colloïden (waaronder EPS), die algemeen bekend staan als membraanvervuilers (Meng et al. 2009).

In dit proefschrift zijn twee benaderingen gevolgd om een hogere membraanflux te bereiken, te weten: het verbeteren van de "slug flow" in buisvormige membranen en de verbetering van de filtreerbaarheid van het slib. Het toepassen van een verbeterde "slug flow" richtte zich op het verhogen van de afschuifkracht op het membraanoppervlak, om de membraanvervuilende bestanddelen van het oppervlak te verwijderen. Het verbeteren van de filtreerbaarheid van het slib richtte zich op het reduceren van het aantal sub-micron deeltjes in de slibvloeistof. Hoofdstuk 2 en 3 laten zien dat de ”slug flow” wel 25 L/m^2.h kan worden zonder verhoging van de transmembraandruk (TMP) over 45 uur. Een veel betere filtreerbaarheid van het slib staat een hoge membraanflux toe. Gebaseerd op deze resultaten concentreren hoofdstuk 4 tot 7 zich op het vinden van een methode om de slib-filtreerbaarheid te verbeteren. Het doseren van coagulant is een veelbelovende aanpak voor het verbeteren van de filtreerbaarheid van slib. Door het toepassen van zowel ”slug flow” als een coagulant zou een beheersstrategie voor membraanvervuiling ontwikkeld kunnen worden. Dit wordt geadviseerd voor vervolgstudies.

8.2 Schuifspanning en filtreerbaarheid

In eerder uitgevoerd onderzoek was er een dilemma wat betreft de tegenstrijdige ideeën met betrekking tot de toegepaste schuifspanning en de slib-filtreerbaarheid. Men nam aan dat een hoge schuifspanning op een membraanoppervlak zorgde voor een makkelijke manier om vervuilingen van een membraanoppervlak te verwijderen. Op deze manier kan membraamvervuiling worden tegengegaan. Echter de slib-filtreerbaarheid kan ook worden verminderd door deze toegepaste hoge schuifspanningen, omdat het voor een verkleining van de deeltjesgrootte kan zorgen. Een verkleinde deeltjesgrootte draagt bij aan de membraanvervuiling (Jeison et al. 2009). Het blijft daarom onzeker of een hoge of juist een lage schuifspanning moet worden toegepast.

Door het optimaliseren van de spuitopening, de gassnelheid en de diameter in het buisvormige membraan van een AnMBR, kunnen geoptimaliseerde schuifspanningen tot 15 Pa worden toegepast op het membraanoppervlak, gebruikmakend van een ”slug flow” (hoofdstuk 2 en 3). Bij toepassing van een geoptimaliseerde schuifspanning was het verkrijgen van een hoge flux van 25L/m^2.h afhankelijk van de slibfiltreerbaarheid. Bij toepassing van deze schuifspanning op het membraanoppervlak met een constante flux was de slib-filtreerbaarheid sterk afhankelijk van de transmembraandruk. Tijdens het onderzoek is in een langdurige experiment van 100 dagen verder aangetoond dat een “slugflow” gebaseerde schuifspanning van 20 Pa in de bulk sliboplossing resulteerde in een stabiele deeltjesgrootteverdeling (hoofdstuk 3).

De beschreven resultaten laten zien dat een geoptimaliseerde “slug flow” kan resulteren in een hoge membraanflux van 25 L/m^2.h met maar een zeer geringe verhoging in de TMP, mits de slib-filtreerbaarheid is geoptimaliseerd. Het verdient daarom aanbeveling om toekomstig onderzoek te richten op de verbetering van de slib-filtreerbaarheid in plaats van op het reguleren van de schuifspanning, waardoor het schuifspanningsdilemma kan worden vermeden. De rest van dit proefschrift behandelt de verbetering van de slib-filtreerbaarheid door middel van het toevoegen van adsorptiemiddel en coagulant.

8.3 Haalbaarheid van adsorptie

Het is aangetoond dat de toevoeging van een adsorptiemiddel (gewoonlijk PAC of zeoliet) aan aerobe MBRs kan helpen om membraanvervuiling te verminderen (Meng et al. 2009). Echter, de PAC zal uiteindelijk zijn effectiviteit verliezen en zal vervangen moeten worden. In het onderhavige onderzoek is PAC ook toegepast in een AnMBR (hoofdstuk 4), hoewel het effect vrij beperkt bleek onder de onderzochte omstandigheden. Met het oog op het feit dat de verversing van de PAC resulteert in slibverlies, en anaerobe micro-organismen erg langzaam groeien, is de toepassing van PAC voor het reguleren van membraanvervuiling in AnMBRs dubieus.

Om gebruik te maken van het positieve effect dat de dosering van adsorberende stoffen kan hebben moet tegelijkertijd slibverlies worden voorkomen tijdens de vervanging van de adsorberende stoffen. Tijdens het onderzoek is een gemagnetiseerde adsorberende stof gemaakt en zijn effectiviteit getest in het verminderen van membraanvervuiling (hoofdstuk 4). Tegen de verwachting in laten experimenten zien dat de toegepaste gemagnetiseerde absorberende stof de filtreerbaarheid van het slib significant verminderde. Zeer waarschijnlijk kan dit worden toegeschreven aan het feit dat de gemagnetiseerde adsorberende stof in de colloïdale vorm voorkwam. Daarnaast resulteerde het verwijderen van de gemagnetiseerde adsorberende stof alsnog in een significant slibverlies. De geobserveerde beperkingen limiteren de bruikbaarheid van het voorgestelde procedé.

8.4 Invloed van coagulatie op de membraanvervuiling

Coagulatie kan effectief zijn in het verminderen van de hoeveelheid fijne (sub-micron) deeltjes in de oplossing en kan daarom worden gebruikt als voorbehandelingsmethode om de membraanvervuiling te verminderen. Er is nader onderzoek verricht naar de mogelijkheid om de natriumionen in zout afvalwater te gebruiken om coagulatie te induceren in een AnMBR (hoofdstuk 5 en 6). Dit zou het gebruik van een externe coagulant kunnen voorkomen. In hoofdstuk 5 wordt aangetoond dat de coagulatie van de sub-micron deeltjes in niet-zout slib significant wordt verbeterd door het zoutgehalte te verhogen. Dit suggereert de mogelijkheid dat de natriumionen in zout afvalwater inderdaad gebruikt kunnen worden om membraanvervuiling te verminderen. Echter, uit de resultaten beschreven in hoofdstuk 6 blijkt dat, ofschoon het verhogen van het zoutgehalte in niet-zout slib helpt om membraanvervuiling te reduceren, het zoutgehalte in zout afvalwater niet hetzelfde resultaat bereikt. Natrium kan alleen dienen als effectief coagulant als de toevoeging gepaard gaat met een significant verschil in de ionsterkte. Het louter verhogen van de turbulentie van een met natrium verzadigd slib zal dus niet leiden tot coagulatie. Derhalve kan worden geconcludeerd dat hoge zoutgehaltes niet bijdragen aan het verminderen van de membraanvervuiling in slib met hoge zoutconcentraties. Bovendien wordt de slechte slib-filtreerbaarheid ook toegeschreven aan de geringe vloksterkte van zout slib.

Uit het onderzoek gepresenteerd in hoofdstuk 5 en 6 kunnen we concluderen dat het niet mogelijk is om natriumionen in zout afvalwater te gebruiken om membraanvervuiling te reguleren. Daarom is het toevoegen van een externe coagulant noodzakelijk om de hoeveelheid sub-micron deeltjes in zout slib te verminderen met het doel de slib-filtreerbaarheid te verhogen. Er werd vastgesteld dat de puls-dosering van een aluminium coagulant effectief is in het verhogen van de slib-filtreerbaarheid (hoofdstuk 7). Een duurexperiment van één maand liet echter zien dat na zo'n coagulant puls-dosering de TMP toch langzaam toenam. Concluderend kan daarom worden gesteld dat de op aluminium gebaseerde coagulanten niet erg effectief zijn voor de regulering van de membraanvervuilingen op lange termijn omdat ze blijkbaar hun coagulatie-eigenschappen geleidelijk verliezen. Daarnaast blijven de sub-micron deeltjes continu vrijkomen tijdens de bio-processen. Verversing van de coagulant is daarom absoluut noodzakelijk. De toevoeging van coagulant verminderde de slibactiviteit enigszins, terwijl de gemiddelde slibdeeltjesgrootteverdeling toenam en de coagulant werd gedetecteerd op het oppervlak van de slibdeeltjes. Gebaseerd op deze resultaten kan coagulantdosering gezien worden als een mogelijke methode voor het reguleren van membraanvervuiling (onder de onderzochte omstandigheden). Bovendien werd door het gebruik van chemische toevoegingen de specifieke methanogene activiteit (SMA) van het zoute slib verhoogd van 0.40 ± 0.03 g COD CH_4/g VSS.d, tot 0.70 ± 0.04 g COD CH_4/g VSS.d,. Van de geteste chemicaliën verhoogde de compatibele oplosstoffen (osmoregulatoren) glycine betaine en Ni^{2+} de SMA van het zoute slib met bijna 100%, terwijl de toegepaste doseringen van K^+, Fe^{2+}, en Co^{2+} of geen effect of een minder significant effect op de SMA lieten zien.

8.5 Aanbevelingen voor toekomstig onderzoek

De combinatie van het toepassen van "slug flow" en het ladingsgewijs toevoegen van een aluminium coagulant geeft de mogelijkheid tot bedrijfsvoering van een AnMBR bij een hoge flux (50 L/m^2.h) en een lage TMP (< 80 mbar) gedurende een korte periode van maximaal een maand. Echter, gezien het feit dat sub-micron deeltjes blijven vrijkomen tijdens een langdurige procesvoering moet er een slimme doseringsstrategie voor coagulant worden ontwikkeld, met de volgende kenmerken:

a) Automatische herkenning van het optimale tijdstip voor coagulantdosering dan wel verversing, en het voorkómen van coagulantaccumulatie in de AnMBR. Waarschijnlijk kan dit worden gebaseerd op een kritische TMP-toenamesnelheid of een drempelwaarde voor sub-microndeeltjes, gevolgd door de verversing van de coagulant.

b) Het voorkomen van regelmatige verversing van de coagulant, omdat zulke verversingen resulteren in een significant slibverlies. Regelmatige verversingen kunnen leiden tot een ontoelaatbaar verlies van methanogeen slib, wat kan leiden tot een verlaging van het zuiveringsrendement of zelfs tot procesinstabiliteit.

8.6 Referenties

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Nomenclature

A	Hamaker constant
a	particle radius
C	floc strength constant
C_{sI}	substrate concentration in the liquid
C_{si}	substrate concentration at the interface
C_{iw}^{sat}	saturation concentration of the organic compound in pure water
$C_{iw,salt}^{sat}$	solubility of the organic compound in water under saline conditions
d	average diameter of floc
d_m	diameter of tubular membrane
d_h	equivalent hydraulic diameter
d_p	particle diameter
d_{pi}	pipe diameter
D	diffusion coefficient
e	charge
G	velocity gradient
J	membrane flux
J_s	surface substrate flux
k	Boltzmann constant
K_I	mass transfer coefficient at particle surface
K_{is}	Setschenow or salting constant
K_s	half saturation coefficient
L	length of tubular membrane
M_i	concentration of component i
N_a	Avogadro number
n	stable floc size exponent
R_e	Reynolds number
R_i	radius of particle i
R_{ir}	irreversible fouling resistance
R_j	radius of particle j
R_m	membrane resistance
R_r	reversible fouling resistance
s	distance between two spherical particles
S	substrate concentration in bioreactor
S_c	Schmidt number
Sh	Sherwood number
Sh'	local Sherwood number
S_i	fragmentation rate
T	absolute temperature
V	mean fluid velocity in the flow channel
V'	local velocity of bulk liquid near the membrane surface
V_a	van der Waals interaction energy
V_t	total free energy between spherical colloids
V_r	repulsive free energy

X	biomass
Y	yield coefficient
Z_i	valence of component i.
$[salt]_{tot}$	total molar salt concentration
δ_s	thickness of the liquid boundary layer
Δp	TMP
$\Delta \pi$	osmotic pressure
φ	zeta potential
κ	reciprocal of Debye length
α	constant
β	coagulation collision frequency
k	mass transfer coefficient at membrane surface
ε	permittivity
ε_h	homogeneous turbulent energy dissipation rate in a stirred tank
ε_a	average energy dissipation rate
ε_0	permittivity of free space
ε_r	dielectric constant
ε_c	critical turbulent energy dissipation rate
ŋ	dynamic viscosity
η	kinematic viscosity
μ_m	maximum specific growth rate
γ	shear rate

Abbreviations

AnMBR	anaerobic membrane bioreactor
COD	chemical oxygen demand
EDX	energy-dispersive X-ray spectroscopy
EPS	extracellular polymeric substance
ESEM	environmental scanning electron microscope
MBR	membrane bioreactor
PAC	powdered activated carbon
PSD	particle size distribution
SMP	soluble microbial product
SMA	specific methanogenic activity
TMP	transmembrane pressure
TSS	total suspended solid
VFA	volatile fatty acid
VSS	volatile suspended solid
FTIR	Fourier transform infrared spectroscopy
CFD	computational fluid dynamic
SBR	sequential biological reactor
UASB	upflow anaerobic sludge blanket
CSTR	continuous stirred tank reactor
PIV	particle image velocimetry
EGSB	expanded granular sludge bed
SRT	solid retention time
NaCl	sodium chloride

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Curriculum Vitae

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