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Influence of cleaning frequency and membrane history on fouling in an anaerobic membrane bioreactor

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Abstract

Membrane fouling was evaluated in a side stream anaerobic membrane bioreactor (AnMBR) operated for the treatment of swine manure. The AnMBR consisted of an external tubular polyethersulphone ultrafiltration membrane module (diameter = 12 mm) connected to a six-liter mixed bioreactor. The system was operated for 135 days without chemical membrane cleaning resulting in a membrane flux of 5–10 L/m² h. Membrane fouling was dominated by a loosely attached fouling layer, which could be removed by flushing the tubular membrane. Intensive chemical cleaning after the 135 days of continuous operation resulted in an irreversible resistance of 3×10¹² 1/m, equivalent to 1.3 times the resistance of the new membrane. More frequent chemical membrane cleaning using HNO₃ could not prevent the development of irreversible fouling. Equilibrium calculations and scanning electron microscopy with energy dispersive spectroscopy demonstrated that inorganic precipitation contributed to fouling of the membrane surface and in the membrane pores.

Keywords: Anaerobic membrane bioreactor; AnMBR; Fouling; Membrane history; Cleaning; Swine; Manure

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1. Introduction

The application of membranes in anaerobic membrane bioreactors (AnMBR) can allow for more reliable and more compact anaerobic treatment compared to conventional anaerobic technologies, provided that detrimental membrane fouling can be prevented. Over the past 15 years, the use of membranes in biological waste treatment processes has become well established, but most of the applications have been aerobic membrane bioreactors [1]. In aerobic membrane bioreactors, aeration can be used to reduce membrane fouling, for example, by using coarse bubble aeration within submerged membranes or by introducing slug flow in external membrane modules [2]. In anaerobic bioreactors, the introduction of oxygen would interfere with anaerobic biological processes and alternative approaches to reduce fouling have to be employed. Furthermore, water chemistry and fouling mechanisms may differ substantially in aerobic and anaerobic systems. For example, precipitation has been reported as a significant fouling mechanism in AnMBRs [3–6], whereas this is not generally a concern for aerobic membrane bioreactors. AnMBRs are promising since they allow us to utilize the advantages of anaerobic treatment, such as net production of energy and low sludge production, while addressing concerns with conventional anaerobic treatment, such as sensitivity to operational fluctuations and poor settleability of anaerobic biomass [7]. Coupling anaerobic treatment with membrane separation allows for operation at high biomass concentrations and the decoupling of hydraulic and solid retention times.

The design and operation of AnMBRs are influenced greatly by feed water composition. The current study evaluated the treatment of swine manure in which the majority of the organic matter is in the particulate form [8]. When such a waste stream is treated anaerobically, hydrolysis of particles can be expected to be the rate limiting step [9]. The contribution of

particulate matter towards membrane fouling in AnMBRs is not well understood and is most likely system dependent. On the one hand, the formation of a filter cake can increase membrane fouling and high concentrations of particulate matter in the bioreactor can increase the potential for filter cake formation. High shear at the membrane surface can help reduce such negative effects associated with concentration polarization and filter cake formation when operated at suspended solids concentrations of less than 50 g/L [1]. On the other hand, soluble and colloidal matter — rather than particles — have been suggested as major factors leading to membrane fouling [10,11]. Some processes avoid potential problems associated with particulate matter in the feed stream by physical removal of particles from the influent of the reactor [6,12]. For example, Lee et al. [12] treated swine manure in an AnMBR, but removed particles larger than 63 μm from the reactor influent. While particle removal likely facilitates the operation of AnMBRs, it reduces the energy that can be recovered from the waste stream and it requires additional processes to remove and subsequently treat the additional waste stream generated.

Membrane fouling can never be completely avoided and design and operation of membrane bioreactors should be based on strategies aimed at (a) reducing the rate of fouling, (b) using chemical or physical cleaning, and possibly (c) accepting the reduced flux resulting from fouling. In AnMBRs, a key factor necessary to reduce the rate of fouling is to maintain cross-flow velocities larger than 1.5 m/s [13]. The frequency of chemical membrane cleaning should be minimized as cleaning requires membranes to be taken off-line, produces contaminated water to be treated, and can reduce the lifetime of the membrane material. Partial, physical membrane cleaning can be achieved using backwashing or flow reversal [2,14]. During physical cleaning, the membrane does not produce filtrate, but

physical cleaning is fast and membrane units usually do not have to be taken off-line. Thus, physical cleaning can be performed as frequently as every 5 min [15], while chemical cleaning is typically performed in intervals ranging from days to months and even years [15–18]. Economic considerations determine whether the benefits of the increased flux associated with frequent chemical and physical cleaning outweigh costs associated with increased personnel or automation required for cleaning.

Efficient chemical cleaning requires the selection of cleaning agents that target dominant compounds responsible for fouling and that do not adversely affect the membrane itself. In addition, the efficiency of specific cleaning methods, such as caustic solutions, acids, EDTA, enzymatic cleaners, or chlorine can be used to differentiate between mechanisms leading to membrane fouling. Caustic solutions at high concentrations and high temperatures could break bonds between the membrane surface and the fouling material and help solubilize proteins [19]. Acid solutions are effective in dissociating salts in an organic matrix and help dissolve the fouling matrix [20]. EDTA can increase the solubility of metal ions such as calcium, magnesium, manganese, and iron [16,21] and removal of these divalent cations can break the interactions in metal-organic complexes. For example, EDTA has been shown to recover membrane flux for fouling with natural organic matter [22]. Enzymes can be used to solubilize the organic matrix of a fouling layer [23]. Chlorine is effective when fouling of pores with organic material occurs, but it is not recommended for polymeric membranes, especially polyamide surfaces [19]. For an AnMBR treating particle free wastewater from an alcohol fermentation plant, Kang et al. [6] showed that acidic cleaning ($\text{pH} = 2$) was effective and could double the flux when organic membranes were used. Lee et al. [12], studying swine manure treatment in an AnMBR, used

sequential cleaning with alkaline solutions followed by acidic agents with a resulting flux recovery of up to 86% of the original membrane flux. With a range of cleaning methods available, the choice of cleaning method and frequency will depend on system operation (anaerobic or aerobic), type of waste, and desired membrane flux.

In the current research, anaerobic treatment of swine manure with an AnMBR was evaluated for the production of particle free water suitable for subsequent recovery of clean water for reuse and of separate product streams containing nitrogen, phosphorus, and potassium. The purpose of this study was to evaluate the possibility of long-term membrane performance in an AnMBR treating swine waste without any cleaning and to evaluate the influence of cleaning frequency and membrane history on the efficiency of membrane cleaning.

2. Materials and methods

A tubular polyethersulphone ultrafiltration membrane (Weir Envig, Paarl, South Africa) was used in a six-liter AnMBR (Fig. 1). The AnMBR was inoculated with a 1:1:1 (v:v:v) mixture of sludge dredged from a swine lagoon (Rolla, MO, USA), anaerobic granules from an upflow anaerobic sludge blanket (UASB) reactor treating brewery wastewater (Anheuser-Busch, Baldwinsville, NY, USA), and anaerobic sludge from the primary anaerobic sludge digester of the Urbana Champaign Sanitary District North-East wastewater treatment plant (Urbana, IL, USA). The reactor was fed with homogenized swine manure at loading rates of 1 or 2 g VS/(L/day) and a hydraulic retention time of 6 days. The hydraulic retention time was maintained independent of membrane flux by recycling excess permeate back to the digester. The solids retention time was calculated based on biomass wasted and biomass removed during sampling. Swine waste was

collected from the finisher buildings at the Swine Research Farm of the University of Illinois at Urbana-Champaign, Urbana, IL, USA. Further details of reactor operation have been described elsewhere [24]. The main membrane was 12 mm in diameter and 1 m in length with a molecular weight cut-off of 20,000 Daltons. Four test membrane modules were integrated in the recycle loop and allowed for evaluation of cleaning and fouling independent of the main membrane module. The test modules contained 10-cm long, 12-mm diameter tubular membranes made of the same material as the main membrane. The mixed liquor in the AnMBR was pumped through the inside of the membrane using a progressing cavity pump (NM021, Netzsch, Germany) and permeate was collected on the outside. A backpressure valve (Tru-Trol BBKA-CAT2, Trutech, Mars, PA, USA) was used to control the transmembrane pressure. During normal reactor operation, the transmembrane pressure was maintained at 20–70 kPa. The pressure drop over all membrane modules was measured and was typically less than 2%. During reactor operation, the flow rate in the recirculation loop was normally maintained at 600–760 L/h, corresponding to cross-flow velocities of 1.5–1.9 m/s. The main recirculation loop was fed from the digester using a peristaltic pump (L/S7523-60, MasterFlex, Barrington, IL, USA) at 10 L/h. The motivation for this decoupling of the recirculation in the membrane module from the recirculation through the reactor was to reduce foaming resulting from high flow rates entering the digester. Reactor control and online data logging was done using LabView (National Instruments, Austin, TX, USA).

Membrane fouling and cleaning were evaluated based on flux measurements during normal reactor operation and in a parallel identical setup that was dedicated for flux measurements using deionized water or filtered permeate. Filtered permeate was used to avoid possible artifacts

resulting from a change in ionic strength, which by itself can potentially lead to removal of fouling layers. Flux using filtered permeate was measured at 20°C and scaled to the corresponding values at 37°C used in the AnMBR based on change in viscosity [25]. The viscosity of pure water is 1.002×10^{-3} kg/m·s and 0.6963×10^{-3} kg/m·s at 20°C and 37°C, respectively [26]. Thus, flux values measured at 20°C were multiplied by 1.45 to estimate corresponding fluxes at 37°C. Chemical membrane cleaning was performed using 0.5% EDTA combined with 1% Na₃PO₄ (adjusted to pH 10 with NaOH) in deionized water as recommended by the membrane manufacturer or using 0.1 N HNO₃ (pH 2). The main membrane module was cleaned after 135 days by sequential cleaning using HNO₃ and EDTA at 25°C, 37°C, or 50°C. The test modules were cleaned using HNO₃ only. Each cleaning step was performed for one hour. During membrane cleaning, a cross-flow velocity of 1.0–1.5 m/s and a transmembrane pressure of 20–40 kPa were maintained. Cleaning with chlorine was not evaluated as, based on manufacturer information, it would have damaged the polymeric membrane material. Test modules (Fig. 1) were used to evaluate the effect of cleaning frequency and membrane history based on a factorial experimental design (Table 1). Two membranes, one new and one that had been in the anaerobic MBR for 135 days without any chemical cleaning, were cleaned in weekly or monthly intervals.

The total membrane resistance (R , [L⁻¹]) was measured and separated into different components based on the resistance in series model:

$$R = \frac{\Delta P}{\mu \cdot J} = R_m + R_{ir} + R_{rev} + R_g \quad (1)$$

where ΔP is the transmembrane pressure [M·L⁻¹·T⁻²], J is the flux through the membrane [L·T⁻¹], μ is the viscosity of the permeate estimated using the viscosity of pure water [M·L⁻¹·T⁻¹], R_m is the membrane resistance [L⁻¹],

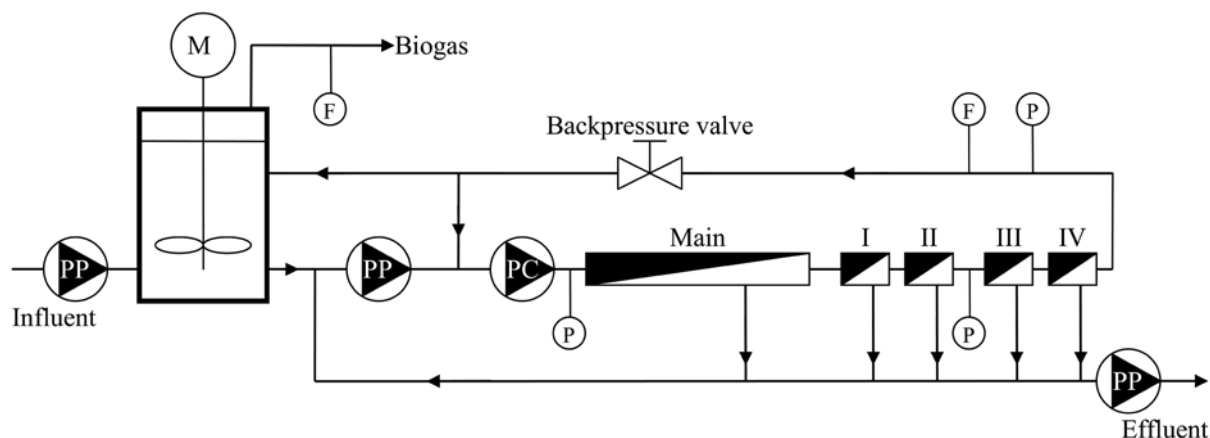


Fig. 1. Schematic of the laboratory-scale anaerobic membrane bioreactor (AnMBR) with one main membrane module (1 m) and four test modules (10 cm) (P = pressure measurement, F = flow measurement, M = mixing motor, PP = peristaltic pump, PC = progressing cavity pump).

Table 1
Factorial design of experiments to evaluate the influence of membrane history and cleaning frequency

	Weekly cleaning	Monthly cleaning
Virgin membrane	Test module I	Test module III
Membrane that had been fouled for 135 days	Test module II	Test module IV

R_{ir} is the irreversible resistance [L^{-1}], R_{rev} is the reversible resistance that can be removed by chemical cleaning [L^{-1}], and R_g is a resistance due to a gel layer resulting from concentration polarization or a loosely attached fouling layer [L^{-1}]. The definition of R_g is an operational definition describing flux recovery due to water flushing [3]. The value of R was calculated using least-squares linear regression of ΔP versus $\mu \cdot J$ and errors of ΔP and J were each assumed to be independent, normally distributed, and with equal variance in the test range. The 95% confidence intervals for R were based on a t -distribution with $n-2$ degrees of freedom (n = number of flux measurements).

The AnMBR permeate was analyzed for magnesium and calcium by atomic absorption spectroscopy (Smith-Hieftje 11, Thermo Jarrell Ash, Franklin, MA, USA). Ammonia and phosphate were measured using a HACH DR4000 spectrophotometer following the Nessler method 8038 and the Molybdovanadate method 8114 (HACH, 2003), respectively. Bicarbonate was measured by titration [27]. pH was measured by a pH electrode (Orion 720A, Boston, MA, USA). The Langelier saturation index of the AnMBR permeate was calculated using the model PHREEQC in which the saturation index is defined as the difference between the measured pH and the hypothetical pH if the solutions were in equilibrium with the solid precipitate [28–30]. A positive value of the saturation index suggests the water is oversaturated and that precipitation likely has occurred or will occur.

Fouling on the membrane surface was visualized after cryosectioning of cross sections. Fouled membranes with and without the adjacent fouling layer before and after cleaning were embedded in optimal cutting temperature (OCT) compounds (Sakura Finetek, Torrance, CA). A Cryocut 1800 (Histotronics Inc., Atlantic, IW) was used to cut cross sections with thicknesses of

60 μm for scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) (FEI Company, Philips XL30 ESEM-FEG, Hillsboro, OR, USA). Samples were dried and coated with carbon by a carbon evaporator (Denton Vacuum Inc., Moorestown, NJ, USA) before SEM-EDS analysis. The peaks in the EDS spectra can identify the presence of possible elements, especially metals with electrons of higher energy [31]. Samples were viewed at 10 kV and 10 mm working distance.

3. Results and discussion

3.1. Overall performance

An overview of membrane and reactor performance is shown in Fig. 2 and Table 2. The main membrane module was operated in the reactor setup without chemical cleaning for 135 days. As a result of fouling, the flux significantly decreased within the first two months of operation from initial values above $100 \text{ L/m}^2\text{h}$ to values in the range of 5 to $10 \text{ L/m}^2\text{h}$ (Fig. 2a). This flux decline can in part be explained by a decrease in the cross-flow velocity in the membrane module (Fig. 2d). After the initial flux decline, the membrane operated at a fairly constant flux for the subsequent four months of operation. The decrease in flux corresponded to an increase in membrane resistance. On day 75, the stator in the progressing cavity pump, which had mechanically degraded, was exchanged for a new stator, resulting in an increase of the cross-flow velocity in the membrane module from 1 m/s to the target value of 2 m/s. This rapid increase in cross-flow velocity resulted in increased mixing and shear, which influenced membrane performance and the biological processes in the AnMBR. In Fig. 2(a) it can be seen that the membrane resistance rapidly decreased from 60 to $20 \times 10^{12} \text{ 1/m}$, most likely due to sloughing or erosion of a loosely attached fouling layer on the membrane surface. This improved membrane performance, however,

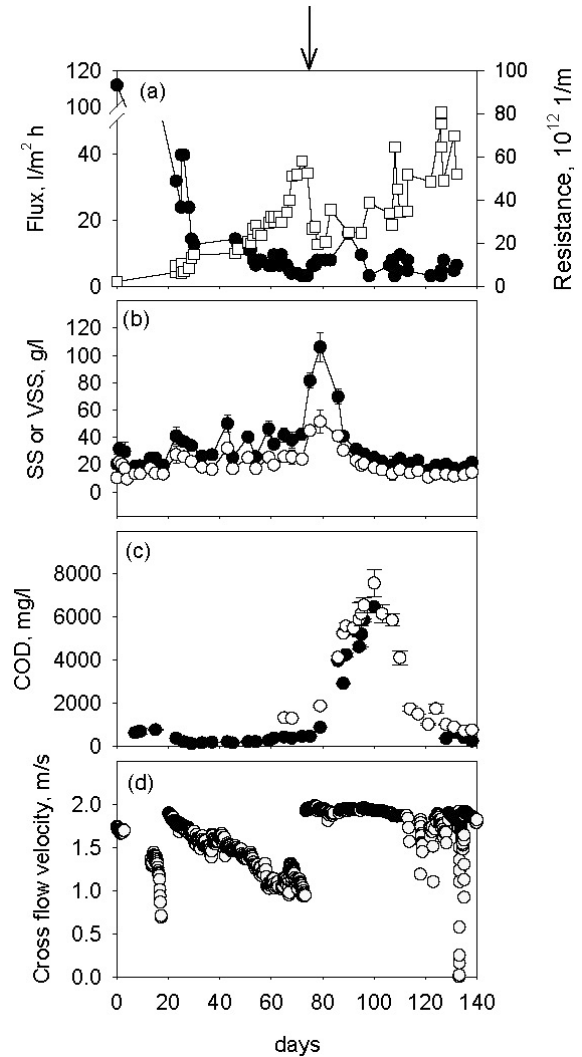


Fig. 2. (a) Membrane flux (\bullet) and resistance (\square), (b) solids in the reactor measured as suspended solids (\bullet) or volatile suspended solids (\circ), (c) soluble COD in the effluent (\bullet) and in the reactor (\circ), and (d) cross-flow velocity in the membrane modules. Arrow indicates the exchange in pump stator resulting in a sudden increase of the cross-flow velocity. Error bars indicate \pm one standard deviation.

coincided with a severe reduction in the biological performance with an accumulation of volatile fatty acids, a decrease in pH, and an increase in effluent COD (Fig. 2c). To avoid a

Table 2
Overall performance of the anaerobic membrane bioreactor (AnMBR)

	Unit	Average (range)	
Water volume in the reactor	Liter	5.0 (4.0–6.0)	
Loading rate	g VS/L/d	1.0	2.0
Solids content	g SS/L	27.0 (15.8–50.0)	49.0 (11.2–106.1)
Ammonia + ammonium concentration	mg-N/L	458.3 (317.2–646.4)	540.2 (317.2–772.5)
VFA concentration	mg acetic acid/L	683.4 (47.2–3241.7)	714.9 (29.7–3583.5)
Biogas production	L/d	2.26 (0.21–5.08)	6.67 (0.92–10.2)
COD removal	%	95.4 (89.7–100)	93.6 (72.0–100)
SRT	Day	118	211
Period of operation	Day	0–52	53–135

complete breakdown of the biological processes, the influent to the AnMBR was stopped from day 98 to day 116 until the biological processes in the reactor stabilized — observed as a decrease in the concentration of volatile fatty acids in the reactor (data not shown). The influence of shear and mixing on substrate conversion, accumulation of intermediates, and the microbial ecology in the AnMBR has been discussed elsewhere [24]. Following the change in pump stator, the cross-flow velocity was between 1.7 and 2 m/s for the subsequent four months and, during that time, the membrane resistance slowly increased from 20 to 70×10^{12} 1/m (Fig. 2a). For cross flow velocities of 1–2 m/s, neither flux nor total resistance appeared to be correlated with velocity (data not shown). On day 135, the membrane was sacrificed for a detailed analysis of the fouling layer. Based on overall reactor performance, it can be concluded that maintaining high cross-flow velocities is critical to limit the rate of fouling. However, even with cross-flow velocities of 2 m/s the membrane resistance slowly increased over time at a rate of 0.7×10^{12} 1/m per day. Sudden changes in shear and mixing can have a detrimental effect on the biological processes in the AnMBR, while these physical changes resulted in improved membrane performance.

The observed fluxes in the range of 5 to 10 L/m²h were comparable to fluxes in other studies evaluating AnMBRs [3,14,32]. In contrast, Lee et al. [12] reported fluxes for an AnMBR in the range of 10 to 30 L/m²h. However, they used a 63 µm filter to pretreat their influent; without this pretreatment, they observed rapid flux decline [12]. Shin et al. [33] achieved a flux of 10 to 30 L/m²h treating swine manure, but they used an MBR operated under aerobic conditions. Full-scale AnMBRs treating swine manure and using the same tubular membrane material as the one in the current study can achieve 15 L/m²h when operated with physical cleaning every two hours [34].

3.2. Quantifying membrane fouling and cleaning

Flux recovery after sequential cleaning of the membrane that had been used in the AnMBR for 135 days is shown in Fig. 3. Flushing the membrane and measuring flux with deionized water resulted in a substantial decrease in the membrane resistance from approximately 60–70 $\times 10^{12}$ 1/m to 26 $\times 10^{12}$ 1/m. Subsequent cleaning with EDTA at pH 10 and NaOH at pH 2 at 25 °C resulted only in a limited further flux recovery. However, the combination of the repeated cleaning and further

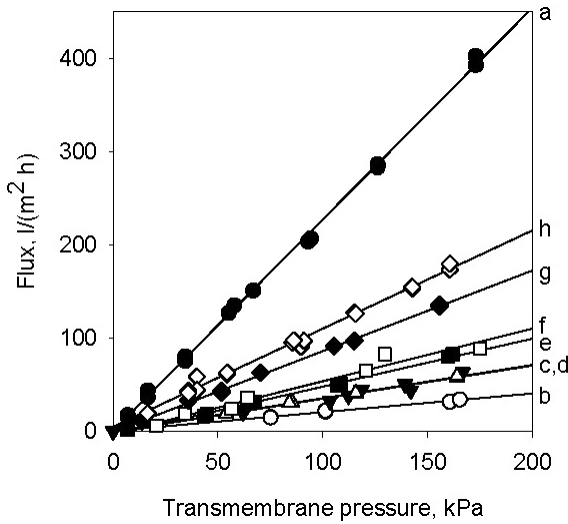


Fig. 3. Sequential cleaning of the fouled membrane after 135 days of operation. Letters refer to flux measured with filtered permeate after sequential steps in the cleaning process: (a) New membrane, (b) fouled membrane, (c) after cleaning with HNO_3 at 25°C , (d) after cleaning with EDTA at 25°C , (e) after long term cleaning with EDTA at 4°C , (f) after cleaning with EDTA at 37°C , (g) after cleaning with EDTA at 50°C , (h) after cleaning with HNO_3 at 50°C .

cleaning at 50°C resulted in a substantial reduction of the membrane resistance to 5.3×10^{12} $1/\text{m}$, which corresponds to 44% of the original clean water flux. Based on the limited flux recovery, it can be concluded that long-term operation without chemical cleaning resulted in residual membrane fouling that was difficult to remove with the chemicals used in this study. This observation raised the question whether more frequent cleaning would have helped to prevent this build up of irreversible fouling. This question is evaluated in Section 3.3.

Different factors contributing to the observed membrane resistance during AnMBR operation were analyzed using the resistance in series model (Fig. 4). The resistance that can be removed using chemical cleaning at 50°C was about 20×10^{12} $1/\text{m}$, leaving a residual resistance

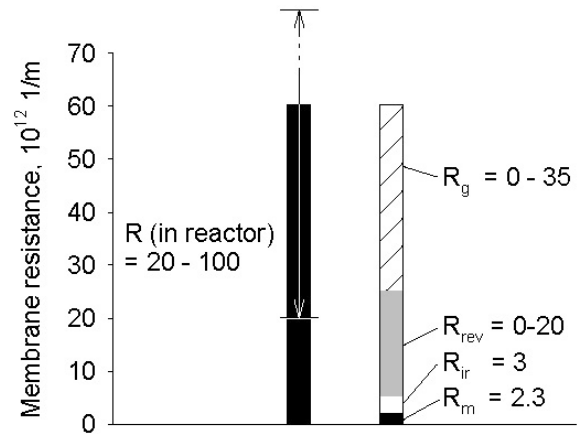


Fig. 4. Contributions of different factors to the overall membrane resistance where R is the overall resistance observed in the reactor. Individual contributions of the membrane resistance are as given in Eq. (1). Numbers with ranges of individual resistances are calculated based on Figs 2 and 3 and are given in 10^{12} $1/\text{m}$.

of 3×10^{12} $1/\text{m}$ due to irreversible fouling and of 2.3×10^{12} $1/\text{m}$ due to the resistance of the membrane itself. Thus, the majority of the membrane resistance developed during reactor operation was reversible and was the result of the formation of a gel layer due to concentration polarization and the formation of a loosely attached fouling layer. During reactor operation, a sudden increase of shear was effective in removing this loosely attached fouling layer (day 75). However, maintaining high cross-flow velocities after day 75 could not prevent a slow but steady increase in membrane resistance in the AnMBR (Fig. 2a). Similar observations have been made with biofilm systems, in which a sudden increase in shear resulted in large sloughing events but high shear stress alone was not able to prevent biofilm development [35]. In fact, biofilms grown under high shear conditions have been shown to be denser and more difficult to remove than biofilms grown under low shear conditions, which accumulate faster but are easier to detach [36].

3.3. Cleaning frequency

The influence of membrane history and cleaning frequency on membrane cleaning is shown in Figs. 5 and 6. Two membranes which had been in the AnMBR for 135 days without cleaning and two fresh membranes were tested with weekly and monthly cleaning intervals (Table 1). For the new membranes, the initial resistances of 2.3×10^{12} 1/m increased for the weekly and monthly cleaning intervals to 4.3 and 4.2×10^{12} 1/m after one month, respectively (Fig. 5a,c). These resistances are only slightly smaller than the resistance of the membrane taken from the AnMBR after 135 days of exposure followed by intensive cleaning (Fig. 3). Thus, irreversible fouling of the membrane is most likely a rapid process that cannot be avoided by weekly chemical cleaning using HNO_3 . The resistance of membranes used in the AnMBR for 135 days was 8.2×10^{12} 1/m and this resistance was reduced to 6.2 and 5.8×10^{12} 1/m with weekly and monthly cleaning, respectively. Thus, for previously fouled membranes there was no apparent benefit to weekly as opposed to monthly cleaning.

Overall, independent of membrane history, membrane resistance after chemical cleaning following one month of exposure ranged from 4.2 to 6.2×10^{12} 1/m, which is similar to the irreversible fouling after long term exposure (Fig. 4). The irreversible resistance of the previously exposed membranes decreased over time, while the irreversible resistance of the new membranes increased. While the overall trend for the tested membranes was clear, the reduction of membrane resistance for individual cleaning events was associated with considerable scatter (Fig. 6a). This scatter could be due to the loosely attached fouling layer that may or may not have detached when measuring the membrane flux before chemical cleaning. Taking this scatter into account, the efficiency of membrane cleaning should preferably be evaluated based on long term observations (Fig. 5) rather than on flux recovery of individual cleaning events (Fig. 6).

From an operational point of view, weekly chemical cleaning seems to provide little benefit. However, monthly cleaning could be beneficial to avoid a slow increase of the membrane resistance as seen in the AnMBR operation in the periods from 0 to 75 and 75 to 135 days (Fig. 2a). This monthly cleaning could be chemical cleaning as discussed in this section or physical cleaning (e.g., short term increase of cross-flow velocity). Unintentional physical cleaning on day 75 during AnMBR operation substantially reduced membrane resistance, but this effect was not studied systematically.

3.4. Composition of fouling layer

Precipitation of inorganic compounds likely contributed to the observed membrane fouling. The saturation index calculated from the AnMBR mixed liquor composition was calculated for likely precipitates using the model PHREEQC (Table 3). A saturation index larger than zero indicates precipitation likely occurred in the reactor and on the membrane surface. Precipitates containing calcium, magnesium, phosphate, and ammonium are commonly found in anaerobic digesters [37] and have also been suggested as dominant foulants in AnMBRs [3–6]. SEM observation of a cross section of the fouled membrane showed a fouling layer of approximately 10–20 μm (Fig. 7a); it should be noted the in-situ thickness may differ somewhat due to the vacuum and drying required for SEM. Chemical characterization of the inorganic compounds using EDS showed that Ca, Mg, and P were present in the fouling layer and at the membrane surface (Fig. 7b). After membrane cleaning using HNO_3 , the fouling layer was removed and the EDS peaks for Ca and P in the membrane surface disappeared (data not shown). Chemical cleaning appeared to be effective in removing the majority of the precipitates. However, this removal was not associated with a complete flux recovery and the observed fouling was most likely due to a

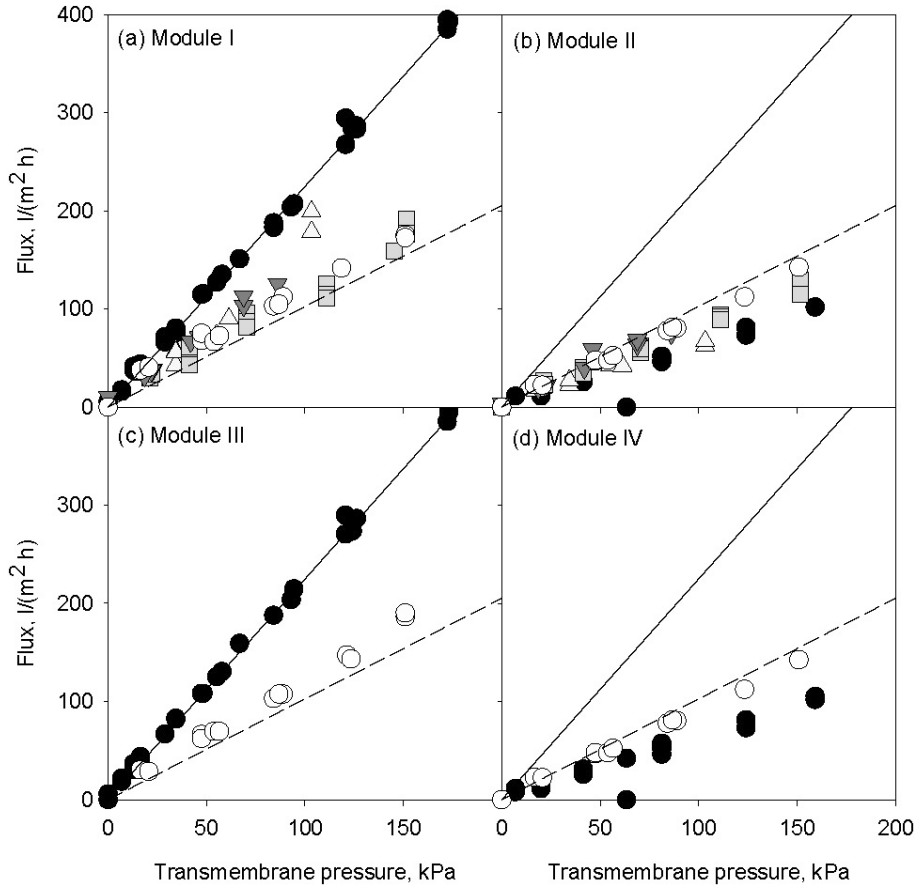


Fig. 5. Flux measured after weekly cleaning for (a) module I, (b) module II, or monthly cleaning for (c) module III, and (d) module IV (Table 1). Data are shown for different times after inserting new membranes into modules I and III: 0 days (●), 7 days (▲), 14 days (▼), 21 days (■), and 28 days (○). Solid line and dashed lines correspond to membrane resistances of 2.3 and $5.3 \times 10^{12} \text{ 1/m}$, which are the average membrane resistances of the clean membranes at 0 days and of all the membranes after 28 days, respectively.

Table 3

Saturation index^a calculated using the model PHREEQC [28–30] at 37°C. A saturation index > 0 suggests precipitation

Phase	Hydroxyapatite	Dolomite	Calcite	Aragonite	Struvite
Compounds	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	$\text{CaMg}(\text{CO}_3)_2$	CaCO_3	CaCO_3	MgNH_4PO_4
$\text{p}K_{\text{so}}$	4.45	17.36	8.56	8.42	13.26
Saturation index	8.57	3.07	1.22	1.08	0.92

^aCalculated based on concentrations measured in permeate from the AnMBR: Mg (4.5 mM), NH_4^+ (43 mM), PO_4^{3-} (2.1 mM), Ca (1.9 mM), and alkalinity (48 mM). The pH was 7.6.

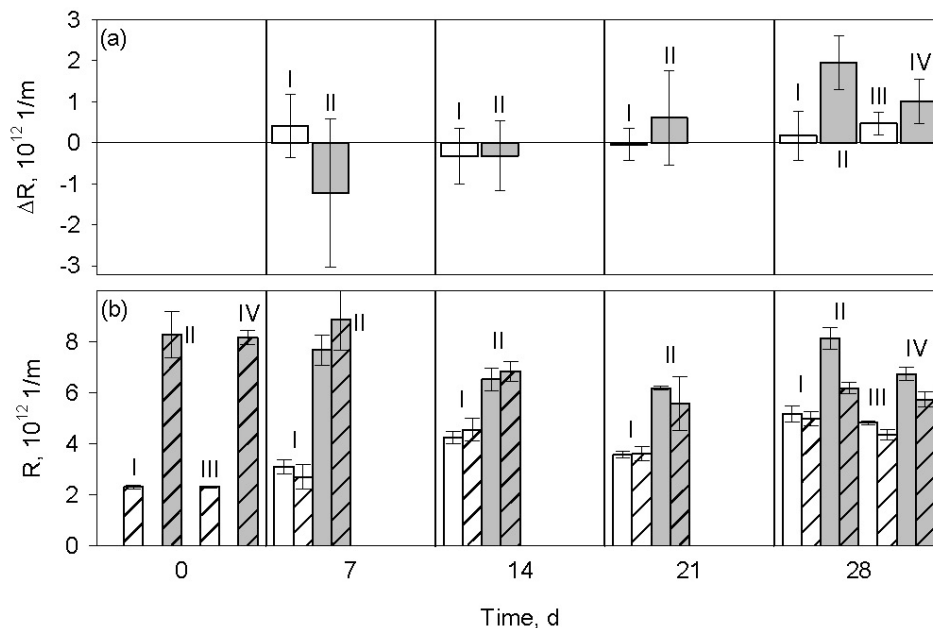


Fig. 6. (a) Decrease in membrane resistance for individual cleaning events, (negative value = resistance increased), and (b) membrane resistance before and after each cleaning event. Labels I–IV refer to the different membrane modules. Solid and hatched bars in (b) refer to the membrane resistance before and after cleaning, respectively. Errors bars are 95% confidence intervals.

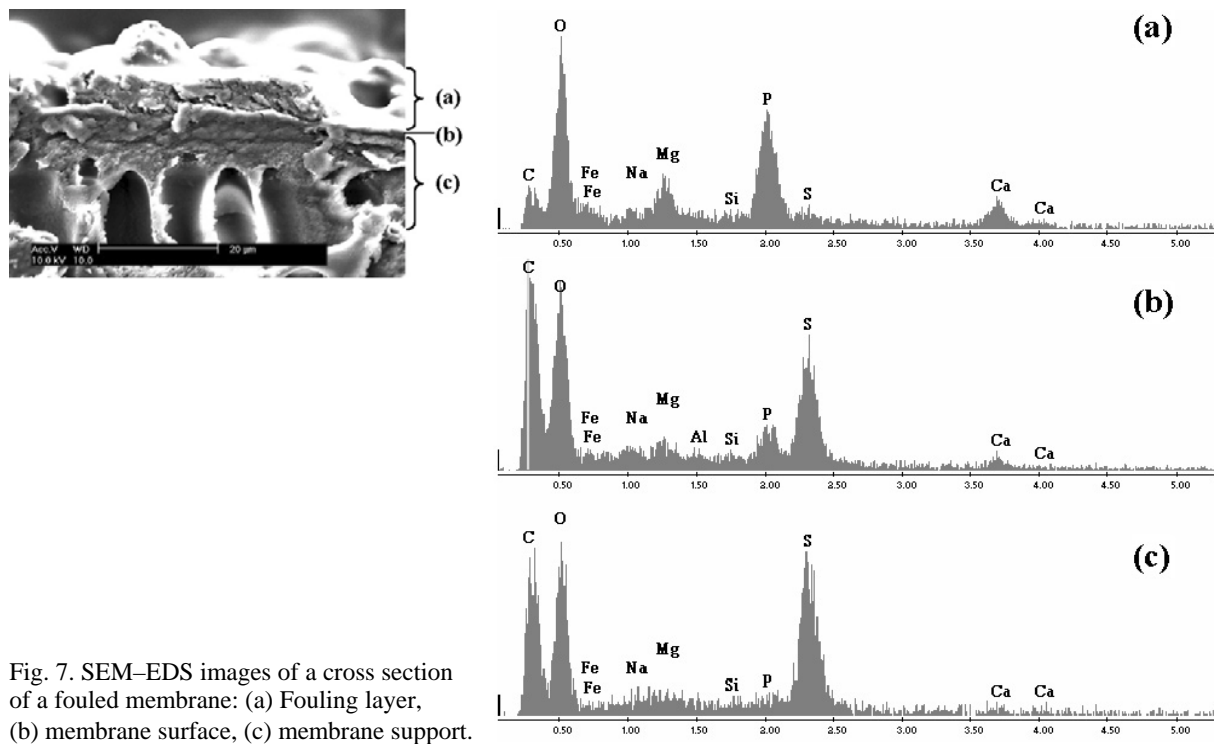


Fig. 7. SEM–EDS images of a cross section of a fouled membrane: (a) Fouling layer, (b) membrane surface, (c) membrane support.

combination of residual precipitation in the pores not observed using EDS and of residual organic foulants. While chemical analysis can verify the presence of specific compounds in membrane fouling, it does not allow quantification of the importance of precipitates relative to other fouling mechanisms such as pore blockage or sorption of organic compounds.

4. Conclusions

Stable operation of an anaerobic membrane bioreactor under low transmembrane pressure (20–70 kPa) and low flux (5–10 L/m² h) was possible for a period of 135 days without membrane cleaning.

A rapid increase in cross-flow velocity after a period of low cross-flow velocity resulted in a substantial decrease in membrane resistance during reactor operation. The increased shear that improved membrane performance was, however, associated with a breakdown of the anaerobic digestion process. Even when maintaining a cross-flow velocity of 2 m/s, the observed membrane resistance slowly increased at a rate of 0.7×10^{12} 1/m per day.

The majority of the observed membrane resistance during reactor operation was reversible and most of the membrane resistance was the result of the formation of a gel layer due to concentration polarization and the presence of loosely attached foulants. Chemical cleaning using HNO₃ reduced membrane resistance leaving a residual resistance of irreversible fouling of 3×10^{12} 1/m (= 1.3 × new membrane resistance).

Membrane history (fresh membrane or 135 days in the AnMBR without cleaning) and cleaning frequency (weekly or monthly) had only a minor influence on the irreversible membrane resistance.

Inorganic precipitation of compounds containing calcium, phosphate, magnesium, ammonium contributed to fouling in and above the membrane

surface. Chemical cleaning with HNO₃ at 50°C removed these inorganic precipitates as observed using SEM–EDS, but this removal did not result in complete flux recovery.

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