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Impact of adding aluminum hydroxyl chloride on membrane flux in an anaerobic membrane bioreactor

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ABSTRACT

Coagulant addition and improved mixing conditions have been used in anaerobic membrane bioreactors (AnMBRs) to improve membrane performance. Before coagulant was added, a flux of 8 L/m² h was applicable and transmembrane pressure (TMP) increased from 1 kPa to 10 kPa in 5 days. However, after the coagulant was added, a flux as high as 50 L/m² h was achieved with no noticeable increase in TMP during six hours of operation. Furthermore, at the same high flux, a long-term experiment showed that TMP increased to approximately 3 kPa in 20 days. Apparently, the applied coagulant significantly improved membrane performance. The reduction in the number of small particles was identified as the main cause for the high flux. However, the number of submicron particles increased in the long-term experiment. In addition, a model was developed that adequately described the TMP development in the short-term and long-term experiments. According to this model, the deterioration in specific cake resistance resulted in a sharp TMP increase in the long-term experiment. In addition, experiments showed that the effect of coagulant on sludge activity was minimal. This study demonstrated that the applied coagulant and reactor operation conditions (mixing properties) have potentials of interest for improving the membrane flux in AnMBR.

1. Introduction

Anaerobic membrane bioreactors (AnMBRs) are reactors that combine anaerobic digestion and membrane filtration. Membranes allow high sludge concentrations in AnMBRs, regardless whether wastewater characteristics and/or process conditions hamper biomass granulation, which is generally the means to ensure high biomass concentrations in anaerobic bioreactors. Therefore, AnMBRs offer higher volumetric conversion capacities compared to other anaerobic reactors that suffer problems with proper sludge retention via granulation or biomass immobilisation. Thus far, AnMBRs have been successfully applied in the full-scale treatment of various complex industrial wastewaters that often have led to operational problems in anaerobic sludge bed reactors [1–3].

AnMBRs are frequently limited by low permeate fluxes. Several authors reported fluxes < 10 L/m² h [4–7]. Many efforts have been done to improve the flux of AnMBRs such as dosing powdered activated carbon (PAC), applying turbulence promoters and gas-liquid two-phase flow [5,8–15]. The effect of dosing PAC on membrane fouling in AnMBR was found to be insignificant [7]. This possibly can be attributed to the fact that PAC gets covered by the biomass and thereby loses its capacity to adsorb foulants and to scour the membrane surface [7]. Alternatively, application of glass beads can significantly reduce membrane fouling, as the beads can shear the membrane surface and thereby preventing the formation of a dense or compact fouling layer. However, the application of glass beads may damage the membrane in long-term operations [13]. The effectiveness of membrane scouring by gas bubbles for fouling control strongly depends on the sludge mobility; a high permeate flux can only be achieved if the sludge mobility is high [16]. In addition, applying ultrasound, which is a known technology for removing foulants from a surface, can improve membrane performance [17]. However, membrane dis-integrity in long-term experiments has been confirmed [18]. This is because ultrasound produces cavitation that damages the membrane [19]. Both the operational conditions and the influent characteristics have a big impact on the attainable flux of AnMBRs, of which the latter can be attributed to the strength and nature or organic pollutants [20–24]. Literature shows that the fluxes in AnMBRs are generally much lower than those obtained in aerobic MBRs [25,26]. Results from full scale reactors showed attainable fluxes of 15–20 L/m².h by applying cross-flow velocities of 1.5–4 m/s [27], which is at the expense of increased energy consumption.

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Coagulant dosing shows interesting perspectives for membrane fouling control. Although several authors reported a positive effect of coagulant dosing [28–30], research on coagulant application in AnMBRs is limited. It was found that dosing polyaluminium chloride was more effective than dosing granular activated carbon for membrane fouling control in an AnMBR [31]. Thus far, results show permeate fluxes between 10 and 20 L/m² h [32,33], which already indicates that similar permeate fluxes might be achieved in an AnMBR compared to an aerobic MBR. Nonetheless, the applicability of AnMBR will drastically improve if fluxes over 30 L/m² h can be achieved [34], which requires a further technology advancement.

In order to achieve a high flux that enables economic reactor operation, the impact of dosing coagulant was further researched in short-term and long-term experiments. A bioreactor was equipped with an inside-out tubular membrane and gas-liquid slug flow. A multi-blade stirrer was applied in the bioreactor for providing suitable mixing conditions for flocculation. As the rheology of anaerobic sludge is significantly different from that of clean water, conventional knowledge on achieving a good flocculation in clean water might be not applicable in this study. The rotation speed of the stirrer was optimized by using computational fluid dynamics to determine ideal mixing conditions. Sludge particle size distribution was measured before and after applying coagulant. In addition, a model was applied to investigate transmembrane pressure development in the short-term and long-term experiments. Furthermore, the impact of dosing coagulant on sludge activity was tested.

2. Materials and methods

2.1. Reactor operation

The inoculum sludge was taken from a full-scale reactor treating saline wastewater from a styrene and propene-oxide production plant (Shell, Moerdijk, The Netherlands). The salinity of the inoculum sludge was 13 g Na⁺/L. A cylindrical glass vessel was used as the anaerobic bioreactor with an effective volume and inner diameter of 4.5 L and 10 cm, respectively. The temperature of the bioreactor was kept at 35 °C via a water jacket surrounding the bioreactor. The reactor feed consisted of a mixture of gelatin, acetate, propionate and butyrate to obtain a chemical oxygen demand (COD) ratio of 2:1:1:1. For the macro and micro nutrient composition, reference is made to one of our previous reports [8]. Sorenson’s phosphate buffer was applied for fixing the pH to 7.2 [35]. NaCl was added to maintain the salinity in the reactor at 13 g Na⁺/L. Details of the composition of the sythetic wastewater can refer to supplementary material. The total suspended solids concentration (TSS) in the AnMBR was 40 g/L. The applied organic sludge loading rate was 0.3 g COD/g TSS.d. A multi-blade stirrer was used for mixing. The rotation speed of the stirrer was fixed at 30 rpm. A tubular inside-out cross flow polyvinylidene fluoride membrane (Norit, the Netherlands) was used and operated in a gas-lift mode. Length and diameter of the tubular membrane were 0.74 m and 5.2 mm, respectively. Permeate flux was regulated by controlling a permeate pump (Watson Marlow 323 D). The produced biogas was injected into the bottom of the membrane via a gas pump (Watson Marlow 323 D). Sludge was introduced into the membrane via gas motion. The gas velocity and the liquid velocity in the tubular membrane were 0.74 m/s and 0.34 m/s, respectively. The trans-membrane pressure (TMP) was recorded by a pressure sensor (AE sensor 261920). Labview was used to record the pressure signal from the pressure sensor. The selected coagulant was aluminium hydroxyl chloride (Pluspac Fd Ach, Feralco). This was done because Fe ions would present in effluent and make the effluent colorful, if an Fe-based coagulant was selected; and an organic coagulant would be degraded by sludge. Coagulant addition was applied in a pulse dose regime, in which the coagulant concentration in the reactor was increased in subsequent steps. After each step, the impact on TMP and membrane flux was assessed. Finally, the highest coagulant concentration, i.e. 0.96 g Al/L was applied in a long-term experiment. A schematic drawing of the setup is shown in Fig. 1.

2.2. Analysis and measurement

Particle size distribution (PSD) was measured with a particle counter (Model 3000, Pacific Scientific Instruments, 2–400 μm). Percentage of each particle size was provided with the particle counter. The number of submicron particles was measured with a HIAC ChemShield instrument (Pacific Scientific Instruments). This instrument uses laser light-scattering as a sensing method for small particle sizes (0.15–0.4 μm). Ion concentration on sludge particles’ surface was measured with energy-dispersive X-ray spectroscopy (EDX, Philips XL30). TSS concentration was measured following standard methods.
2.3. Sludge activity measurement

Specific methanogenic activity (SMA) was measured with an Automatic Methane Potential Test System (AMPTS) (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 TSS/L. In order to obtain a salinity equal to that of the reactor from which the inoculum was derived, the salinity was adjusted to 13 g Na+/L by the addition of NaCl. Each SMA test was performed in duplicate, and an SMA test of a blank sample was also performed. The blank sample was equal to the samples of each SMA test except for the acetate addition. The total volume of the mixture of sludge and medium was 400 mL. The medium was prepared according to one of our previous reports [8].

2.4. TMP model

The TMP in the AnMBR was modelled using Equations (1–6), whereas the definition of parameters and variables used in the Equations (1–6) are shown in Table 1. The Eq. (1) has been widely adopted for describing the relationship between transmembrane pressure and liquid dynamic viscosity as well as flux and total filtration resistance. The total filtration resistance is the sum of membrane resistance and cake layer resistance (Eq. (2)). The cake layer resistance is determined by the specific cake layer resistance and accumulated cake mass (Eq. 3). The Eq. (3) was extended by Eq. (4), considering that a cake layer is compressible [37]. Membrane filtration results in the accumulation of foulants on the membrane surface, while inertial lift forces remove foulants from the membrane surface to the bulk solution. Eq. (5) shows how these two mechanisms influence the variation of foulant mass on the membrane surface.

\[
P_f = \mu R_t \\
R_t = (R_m + R_c) \\
R_c = RM \\
r = r_{co}(1 + \frac{P}{P_0^{\alpha}}) \\
d\frac{M}{dt} = \frac{24CJ^2}{24J + C_dDG} - \frac{\beta(1 - \alpha)GM^2}{\gamma l^2 + M} \\
D = \sum_{i=1}^{n} D_i \times P_i
\]

Detailed explanation for parameters and variables is discussed in literature [37,38]. The size of the suspended anaerobic sludge particles covered a wide range [6]. However, previous studies did not show how the particle diameter, D, was obtained. In this study, statistics was applied to obtain a particle diameter that was applied in the Eq. (5). Then, the mathematical expectation of all the measured particle diameter was applied as a particle diameter as shown in Equation (6).

The average shear rate on the membrane surface was obtained by performing a computational fluid dynamics (CFD) study. For details regarding the CFD study, we refer to our previous report [16]. The model was implemented by using Aquasim 2.0. Transmembrane pressure, \( P_t \), was the sole model output. When applying the Equations (1–6), initial specific cake resistance and compressibility coefficient were estimated by Aquasim 2.0. The compressibility coefficient, alpha, can vary from 0 (non-compressible) to 1 (highly compressible) [37]. In this study, it was estimated to be 0.72. Total suspended solids concentration was measured following standard method [36]. Other parameters were adopted from literature.

3. Results and discussion

3.1. Effect of particle diameter on the accumulated cake mass on the membrane surface

When no coagulant was added, TMP increased quickly (Fig. 2). At a permeate flux of 8 L/m² h, the TMP increased to approximately 12 kPa in seven days. Fig. 2 shows that the model agreed well with the measured data, which indicates that the model could be effectively applied to explain the tubular membrane filtration process. After about 120 h in Fig. 2, the TMP increase was reliably predicted by Equations (1–6), showing that these Equations can be applied to analyze membrane filtration performance. By setting \( dM/dt \) in Eq. (5) to zero, i.e. assuming steady state, a relationship between particle diameter and mass of foulants was obtained (Fig. 3). Fig. 3 shows that particles with diameters below 10 μm most substantially contributed to foulant accumulation on the membrane surface. Other experiments also confirmed that particles with diameters of this size (< 10 μm) are the most important membrane foulants [39].

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
<th>Unit</th>
<th>Note</th>
<th>References</th>
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<tbody>
<tr>
<td>C</td>
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<td>40</td>
<td>kg/m³</td>
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<td>Measured</td>
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<td>J</td>
<td>Membrane flux</td>
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<td>m³/m² s</td>
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<td>Determined by permeate pump</td>
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<td>s⁻¹</td>
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<td>α</td>
<td>Stickiness coefficient</td>
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<td>parameter</td>
<td>[37,38]</td>
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<tr>
<td>β</td>
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<td>–</td>
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<td>[37,38]</td>
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<td>r</td>
<td>Compression coefficient</td>
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<td>Dynamic viscosity</td>
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<td>[37,38]</td>
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<tr>
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<td>parameter</td>
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<td>Percentage of D_0 in the measurement</td>
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<td>–</td>
<td>parameter</td>
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</table>
3.2. Effect of dosing coagulant on the sludge particle diameter

The presence of coagulants will destabilize the small-sized suspended particles, which subsequently will be attracted to each other through electrostatic interactions, forming large flocs. Therefore, aluminum hydroxyl chloride, which is a coagulant, was added to the reactor at a dose of 0.48 g Al/L, after which flocculation occurred. Compared to sludge without coagulant addition, the addition of coagulant resulted in a substantial decrease in the percentages of particles with a diameter below 6 μm (Fig. 4). Meanwhile, the number of particles with diameters between 8 μm and 12 μm increased. In addition, a dose of 0.72 g Al/L further enhanced this effect. The latter dose can be considered the optimum dosage, since the application of a higher aluminum dosage (0.96 g Al/L) resulted into a similar PSD as the application of a lower dosage. The effect of coagulant addition at these dosages on membrane performance were tested afterwards.

3.3. Short-term effects of dosing coagulant on membrane fouling

Fig. 5a shows that a low dose of coagulant (0.48 g Al/L) effectively restrained the increase in TMP when the flux was 15 L/m² h. The TMP was maintained around zero kPa. When a higher flux was applied (30 L/m² h), only a small increasing trend was observed. However, eventually the TMP increased to 12 kPa within 70 h, as shown in Fig. 5b. Therefore, although aluminum hydroxyl chloride apparently improved the membrane performance, it was not possible to achieve a very high flux with low or no TMP increase when a low coagulant dosage was applied.

Therefore, more coagulant was added to reach a dosage of up to 0.72 g Al/L. The membrane filtration performance significantly improved after this dose. Fig. 6a shows that the TMP did not increase at all over several hours even when the flux was as high as 50 L/m² h. Compared to the frequently observed low filterability of anaerobic sludge [42,43], the aluminum hydroxyl chloride addition allowed a very high short-term flux. Subsequently, higher fluxes were applied at the same dose. The TMP was measured as a function of time at various fluxes (Fig. 6b). When the fluxes were lower than 70 L/m² h, the TMP increase rates were small, but a slight increasing trend was observed. A coagulant does of 0.96 Al/L was also tested; however, no further improvement in attainable permeate flux was found (data not shown).

3.4. Long-term effects of dosing coagulant on membrane fouling

Fig. 6 shows that a high flux of 50 L/m² h appeared to be sustainable on the short term. Therefore, an experiment was performed to investigate the TMP trend on the long term. Fig. 7 shows that a low TMP was observed at the beginning of the long-term experiment, although it gradually increased afterward. However, the time for reaching a TMP approaching 10 kPa was greatly extended, compared to the experiments when no coagulant was applied (Fig. 2).

Other AnMBR-related studies obtained fluxes below 20 L/m² h by applying organic coagulants [28,32,33,44]. Our present study showed that dependent on process conditions and type of coagulant, a much higher flux, reaching 50 L/m² h, can be achieved. Furthermore, we believe that the designed hydraulic conditions in our reactor were
favorable for flocculation of particles and hence contributed to the high flux. A multi-blade stirrer with a rotation speed of 30 rpm was applied in our reactor. The shape and the size of the blades as well as the speed were designed for creating optimal conditions for flocculation in the reactor (see Supplementary material). Moreover, the average contact time in the bioreactor was apparently enough for an effective coagulation process. Other studies regarding fouling control in an AnMBR by using coagulants did not address the required hydraulic conditions. Our results clearly indicate that the applied gas-liquid two-phase flow is not the major factor in flux control (Fig. 2); apparently, an increase in sludge filterability is indispensable for flux enhancement [16].

The gradual increase in TMP was attributed to a gradual increase in the number of submicron particles. The submicron particles, referred to as colloids, are considered major membrane foulants [45]. The addition of the coagulant significantly decreased the number of submicron particles from $2.5 \times 10^5$ to $1.7 \times 10^5$ particles per liter. This very likely contributed to the observed increased filterability of the sludge, as witnessed by a higher permeate flux, during the short-term experiments. However, after 30 days, the submicron particle number almost increased to its initial value: $2.3 \times 10^5$ per liter exerting a negative impact on cake permeability. Therefore, an increase in the number of submicron particles should be avoided considering the strong relationship between sludge filterability and the number of submicron particles. The increase in submicron particle number likely can be attributed to bacterial activity. Bacteria continuously produce submicron particles. These biomass-based submicron particles are not completely biodegradable [46]. Therefore, their accumulation in membrane bioreactors is inevitable.

The applied model effectively matched the measured TMP trend. Table 1 and Fig. 7 show that the addition of coagulant reduced $r_{co}$ from $8.1 \times 10^{11}$ m/kg to $1 \times 10^9$ m/kg (see Table 1 and Fig. 7). However, when a constant $r_{co}$ was assumed, the Equations (1—6) could not predict the sharp increase in TMP after 20 days (Fig. 7). Nevertheless, the increase in the number of submicron particles indicated that $r_{co}$ should vary. The model estimated that a linear increase in $r_{co}$ after day 20 resulted in a sharp increase in the TMP, and the simulated TMP nicely matched the measured TMP (Fig. 7). A few parameters in the model are adopted from literature. Although the coagulant might have impacts on these parameter values, the impact is likely to be minimal as the variation in $r_{co}$ could well model the variation in TMP, showing $r_{co}$ is an important factor affecting TMP increase.

### 3.5. Effects of dosing coagulant on sludge activity

We focused on the effects of dosing coagulant on improving membrane performance, while the effects on reactor long-term performance such as COD removal was ignored. Nevertheless, an SMA test was applied to evaluate whether the coagulant had a negative impact on sludge activity. When no coagulant was added, the sludge activity was $0.40 \pm 0.03$ g COD CH$_4$/g TSS.d. The addition of the coagulant only slightly decreased the sludge activity to $0.37 \pm 0.03$ g COD CH$_4$/g TSS.d at 0.96 g Al/L. The small decrease in SMA could result from the accumulation of Al$^{3+}$ on the sludge particle surface (Table 2), which might restrict the substrate mass transfer in the SMA test. Our study
coagulant can be removed from the bioreactor by sludge discharge. Therefore, a long-term experiment (> 1 year) should be conducted to optimize intermittent coagulant addition and ineffective coagulant removal for ensuring sustainable membrane performance. Moreover, except for the advanced control strategy, the impacts of sludge discharge, type of coagulant on membrane performance, operation cost, reactor’s activity, as well as microbial structure, will be evaluated in the long-term experiment.

It should be noted that our present AnMBR experiments were conducted applying TSS concentrations of about 40 g/L, resulting in non-Newtonian fluid behavior, which hampers a direct comparison with most experiments that apply different (Newtonian) hydrodynamic conditions. Nonetheless, results clearly showed an improved membrane performance after reducing the number of submicron particles. In addition, Fig. 3 suggests that the membrane performance is impacted by a shift in PSD between 2–10 μm, which is in accordance to recent research [49].

4. Conclusion

Although the impacts of coagulant addition on fouling control in anaerobic membrane bioreactors have been tested, membrane flux is usually below 20 L/m²·h. This study achieved a significant membrane fouling control effect. TMP was maintained below 3 kPa in 20 days while a high membrane flux at 50 L/m²·h was applied. This flux was much higher than the achievement shown in literature. Moreover, the TMP variation in long-term membrane operation can be reasonably modelled. The deterioration in specific cake resistance was estimated to be the main reason for the TMP jump. Furthermore, the impact of coagulant on sludge activity was negligible. Finally, it is suggested that adding coagulant in anaerobic membrane bioreactor is a promising approach for alleviating membrane fouling and suitable mixing should be applied for promoting the coagulation effect.

Declaration of Competing Interest

The authors report no conflicts of interest.

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Appendix A. Supplementary data

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References


