Use of flocculants for increasing permeate flux in anaerobic membrane bioreactors

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ABSTRACT

Biomass retention, required for high rate anaerobic wastewater treatment, can be accomplished coupling an anaerobic bioreactor with membrane filtration. However, low flux seems to be a common factor when operating anaerobic membrane bioreactors (AnMBRs). Modification of biomass properties may represent a strategy for improving membrane flux. The addition of flocculants was tested as a tool for flux increase. Six different products were tested in dead-end filtration experiments. Based on the results, two products were selected for cross-flow tests. The one presenting better performance (Nalco MPE50) was tested in a laboratory-scale continuous AnMBR. Results show that the flocculant was able to substantially increase flux. Indeed, the flux-increasing effect was observed for several weeks after flocculant addition. Therefore, the use of flocculants seems to be an interesting tool to cope with temporary increases in required flux.

Key words | anaerobic, flocculant, flux, membrane bioreactor

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INTRODUCTION

Aerobic membrane bioreactors (MBRs) have been applied now for two decades for the treatment of sewage and industrial wastewaters. Anaerobic membrane bioreactors (AnMBRs) have also been extensively studied, and several full-scale plants are now under operation. However, maintaining high levels of permeate flux seems to be more difficult to achieve in anaerobic MBRs than in aerobic ones. This is the result of lower filterability of anaerobic biomass (Spagni *et al.* 2010) and the need for higher biomass concentration, due to lower specific activity of anaerobic microorganisms. As a result, most of the reports dealing with the operation of AnMBRs involve much lower fluxes than those reported for its aerobic counterpart (Dereli *et al.* 2012).

Particle deposition seems to be a critical factor determining permeate flux and therefore membrane requirements in AnMBRs (Jeison & van Lier 2007). This phenomenon is determined by suspension properties, together with membrane characteristics and operational conditions. Solids concentration, rheology, hydrophobicity and particle size distribution are properties that have been related with flux-reducing phenomena (Le-Clech *et al.* 2006).

Modification of suspension properties in MBRs for wastewater treatment has been attempted by adding different types of chemicals or additives. Addition of activated carbon or flocculants is the most frequent reported strategy. Both alternatives look for reducing fouling potential of the biomass, by decreasing the concentration of soluble microbial products and/or by increasing particle size, by aggregation or adsorption of small particles and colloids. Particle size distribution can strongly determine solids deposition over the membrane surface. Indeed, the magnitude of back-transport mechanisms, such as shear-induced diffusion and inertial lift, are strongly related with particle size (Belfort *et al.* 1994; Tardieu *et al.* 1998). This explains why smaller particles experience a higher tendency to deposit over the membrane surface than larger ones (Kromkamp *et al.* 2002).

The use of flocculants has been extensively tested in aerobic MBRs with promising results (Yoon & Collins 2006; Koseoglu *et al.* 2008; Meng *et al.* 2009; Huyskens *et al.* 2012). Indeed, commercial products are available in the market specifically oriented for MBRs for aerobic wastewater treatment (Wozniak 2010). However, available information for anaerobic MBRs is limited. Powdered activated carbon addition has been reported for AnMBRs, with different results (Hu & Stuckey 2007; Akram & Stuckey 2008; Vyrides & Stuckey 2009). Recently, magnetic

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absorbents were also tested in AnMBR, with unsuccessful results (Yang *et al.* 2012). To the knowledge of the authors, no reports are available dealing with the use of flocculants for flux enhancement in AnMBRs. This research was focused on the evaluation of different flocculants as an alternative to improve operational flux in a laboratory-scale AnMBR.

MATERIALS AND METHODS

During this study, six different flocculants were evaluated in terms of their potential capacity for increasing permeate fluxes. Tested flocculants were:

- cationic polymers MPE30, MPE50 and MPE51 from NALCO;
- two experimental flocculants developed by NALCO, which will be referred to as P1 and P2;
- TEC-200, a copolymer based on polyacrylamide and sodium acrylate produced by SNF Floerger, obtained from a local supplier.

Flocculants were evaluated following a three-step process. In the first place, dead-end filtration experiments were performed, in order to evaluate the changes in specific cake resistance (α) derived from different flocculant dosing levels. Determination of α is a simple measurement, not requiring advanced equipment, and generating results in a matter of minutes. It represents the resistance to permeation of the deposited particles, which is related to suspension particle size distribution. Then, it is inferred that it can be used to compare filterability and then flocculant dosage effect. Based on previous results, two flocculants were selected. Flux-increasing capacity of the two selected flocculants was then tested in a cross-flow filtration unit equipped with a 40 cm tubular inside/out membrane. Flocculants were evaluated in terms of their critical flux enhancement capacity. Finally, one flocculant was selected based on its performance during cross-flow experiments, which was further tested during the operation of a 4.5 L AnMBR equipped with an external inside/out tubular membrane.

Dead-end and cross-flow filtration experiments were performed using a sludge suspension prepared by disintegrating anaerobic granular sludge, using a domestic blender. Anaerobic granular sludge was collected from a full-scale upflow anaerobic sludge blanket reactor treating brewery wastewater. Filtration tests were performed at total suspended solids (TSS) concentration of 9 g/L. Initial solids concentration in the AnMBR when testing the selected flocculant was 28 g TSS/L.

Dead-end filtration tests

Specific cake resistance of sludge samples was measured in an unstirred batch filtration unit, containing a single outside/in microfiltration membrane, with 0.2 μm pore size. Membrane tube dimensions were 5 cm length and 0.9 cm diameter. The membrane was placed in a 25 mL useful volume cylindrical glass module that contained the sludge. Measurements were performed at room temperature (18–22 °C). Filtration was performed at a constant flux of 30 L/(m^2 h), by means of a peristaltic pump that collected the permeate from the membrane lumen. Trans-membrane pressure (TMP) was continuously measured by a pressure sensor located in the permeate line. To avoid sludge settling, nitrogen was gently bubbled into the filtration unit. Previous experiments determined that the bubbling of nitrogen did not produce significant shear over the membrane surface, so filtration could be still considered dead-end. α was determined with the observed TMP evaluation over time, using dead-end filtration equations for constant flux operation:

$$\mathrm{TMP} = \frac{\eta \cdot \alpha \cdot C \cdot J}{A} V + \eta \cdot R_M \cdot J \quad (1)$$

where η represents permeate viscosity, C the solids concentration, J the permeate flux, A the membrane area, V the permeate volume and R_M the membrane resistance.

Cross-flow filtration tests

Cross-flow filtration tests were performed using a membrane module fitted with a single inside/out tubular membrane of 30 nm pore size (X-Flow, Norit, The Netherlands). Membrane dimensions were 0.5 cm diameter and 35 cm length. The required TMP was provided by applying vacuum to the permeate side of the membrane, by means of a peristaltic pump. TMP was measured by a pressure sensor located in the permeate line. The membrane module was connected to a 250 mL glass vessel containing sludge. Nitrogen gas was injected in the bottom of the membrane to generate a gas/liquid mixture inside the membrane tube. Liquid recirculation between the sludge vessel and membrane module was brought about by the resulting gas-lift effect. Nitrogen gas was injected at a rate producing a gas superficial velocity of 0.3 m/s. Critical flux was measured in this set-up, using sludge samples with different dosages of flocculant. Critical flux was determined by the flux step method, as described by Jeison & van Lier (2007). The filtration module was operated at room temperature.

In order to evaluate floc stability over time, flocculated sludge samples were stored in a 1 L glass bottle for 2 weeks. Mixing was provided continuously by means of nitrogen gas bubbling. Sludge was taken from this reservoir and critical flux was measured every day in order to determine its evolution over time.

AnMBR operation

A laboratory-scale AnMBR was operated to test the effectiveness of the selected flocculant on permeate flux. AnMBR was composed of a 4.5 L bioreactor connected to an external membrane module containing a single inside/out 70 cm long tubular membrane of the same characteristics as that used during cross-flow filtration tests. Sludge circulation between the bioreactor and the membrane module was the result of the gas-lift effect, generated by biogas injection in the membrane bottom, as was also the case of the set-up for cross-flow filtration tests. Applied gas superficial velocity in the membrane tube was 0.3 m/s. A detailed description of the reactor can be found in Torres *et al.* (2011). The reactor was continuously operated using a synthetic wastewater with ethanol and peptone as source of chemical oxygen demand (COD). Nutrients were also provided, as well as sodium bicarbonate as a buffer. Ethanol and peptone were added in order to provide 70 and 30% of total COD, respectively. The reactor was operated at an organic loading rate of approximately 7 g COD/(L d). Whenever necessary, excess permeate was continuously returned to the reactor in order to keep constant the hydraulic retention time. The selected flocculant was dosed only on day 22 of operation.

Analytical methods

Suspended solids and COD were determined by standard methods (APHA *et al.* 1998). Particle size distribution was measured by laser diffraction (Shimadzu SALD3101).

RESULTS AND DISCUSSION

Dead-end filtration experiments revealed that all tested flocculants indeed achieved reductions in specific cake resistance of suspended anaerobic sludge, as can be seen in Figure 1. Tested dosing levels were in the range 0–900 mg/L for a sludge sample containing around 9 g TSS/L. Even though different flocculant dosages resulted in differences in particle size distribution, results were not conclusive, not observing a clear tendency that could be related with values of α changes (data not shown). Particle size is related in a complex way with filtration performance. It impacts the back-transport phenomena (diffusion, shear-induced diffusion and inertial lift). As a result, particle size determines the level of particle deposition and the resistance of the deposited particles to the permeate flow, affecting the value of α. Moreover, in a heterogeneous suspension such as biological sludge, not all the particles behave in the same way, since small particles will have a higher tendency to deposit on the membrane surface, when surface shear is induced.

The original sludge sample (9 g TSS/L) presented a α value of 5.2×10^{13} m/kg. Only four flocculants were able to reduce α value below 1×10^{12} m/kg: P1 (at 700 mg/L), MPE30 (at 300 mg/L), MPE50 (at 300 mg/L) and MPE51 (at 300 mg/L), as can be observed in Figure 1. However, MPE50 and MPE51 were the additives providing the higher reduction of α. Therefore these two were selected for continuing with cross-flow tests.

During cross-flow filtration experiments, MPE50 and 51 were both tested at a concentration of 300 mg/L, a value selected based on α measurements (Figure 1). Figure 2 presents critical flux determinations performed daily, for a 2 week period to evaluate stability of the flocs. MP50 was able to induce a 100% increase in critical flux. Moreover, critical flux was stable for 10 days, showing a decreasing tendency only during the last 2 days. MP51 on the contrary decreased critical flux (Figure 2). MPE51 produced big flocs that showed the tendency to stick to each other and to the tube walls, obstructing the membrane lumen. This produced a dramatic decrease in liquid circulation. It has to be remembered that liquid circulation in the cross-flow filtration unit was induced by gas-lift effect and no liquid pumping was applied, in order to prevent high shear forces that could promote floc disintegration. This means that MPE51 may not be suitable for inside/out tubular membrane filtration in absence of forced sludge circulation over membrane tubes, as was the case of the tested configuration. On systems involving pump-driven sludge circulation this may not be a problem. Moreover, MPE51 may be of interest when working with submerged systems; however, further tests are needed to confirm this hypothesis.

Considering the observed performance of MPE50 during daily critical flux determinations, this flocculant was selected for testing in the continuous AnMBR. Results shown in Figures 1 and 2 were obtained using sludge samples formed by disintegrating anaerobic granules. In order to determine

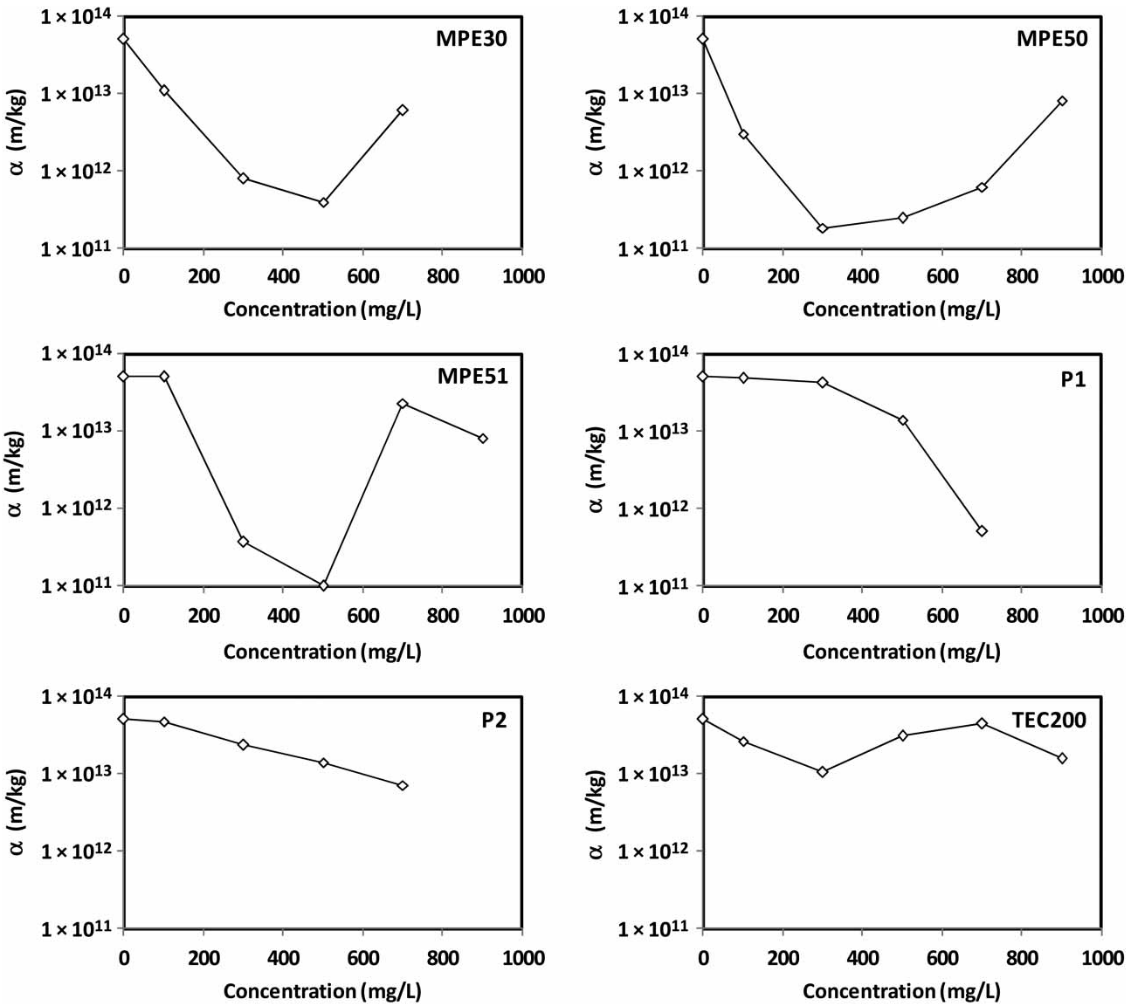

Figure 1 | Specific cake resistance of the sludge after application of different dosages of the tested flocculants.

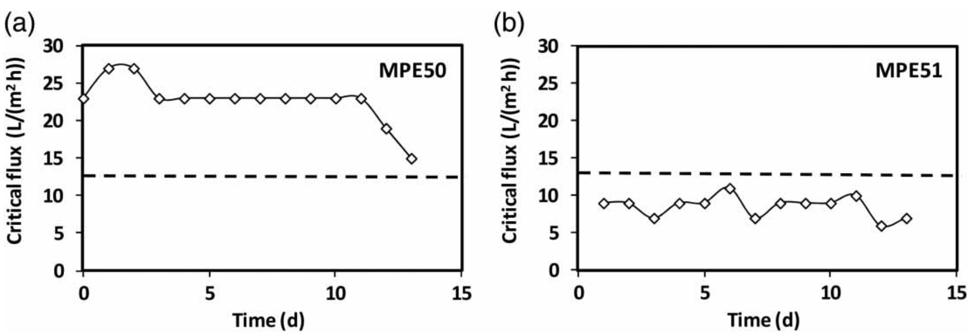

Figure 2 | Stability of the flocs formed by flocculants MPE50 (a) and MPE51 (b), expressed as evolution of critical flux. Dotted lines indicate the critical flux of the original sludge. Flocculant dosage: 300 mg/L, solids concentration: 9 g TSS/L.

the correct dosage for the sludge contained in the AnMBR (28 g TSS/L) new α measurements at different dosages of MPE50 were performed. Results are presented in Figure 3. The original anaerobic sludge α was 2.2×10^{14} m/kg. Based on the observed values of α, an MPE50 dosage of 1,500 mg/L was selected to be applied to the AnMBR. This value was selected since further increase in flocculant concentration did not produce a relevant decrease in α. The chosen flocculant

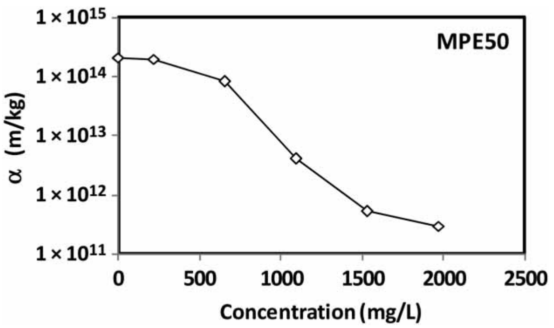

Figure 3 | Specific cake resistance of the sludge from AnMBR after application of different dosages of MPE50.

dosage enabled a specific cake resistance reduction of two orders of magnitude, down to 5×10^{11} m/kg. This latter value falls within the range reported for sludge developed in aerobic MBRs (Ahmed *et al.* 2007; Khan *et al.* 2009).

The AnMBR reactor was operated applying an on-line flux control strategy, which keeps the operational flux at a value in the range of the critical flux. On-line flux control is based on TMP evolution during successive filtration cycles, and reduces or increases the applied flux in order to keep low or no pressure increase during each filtration cycle. More details can be found in Jeison & van Lier (2006). Critical flux prior to flocculant addition was 4–5 L/(m^2 h).

Applied flux and filtration resistance during reactor operation are presented in Figure 4. Flocculant was added on day 22, producing a large increase in flux, up to close to 40 L/(m^2 h). However, flux decreased fast during the next 48 hours down to 20 L/(m^2 h). Then, flux declined gradually during the following 4 weeks, most likely as a result of floc disintegration. COD removal rate was stable, in the range 98–99%, during the whole reactor operation, indicating the absence of inhibition or toxic effect. Flux stayed at a value over 10 L/(m^2 h) (twice the value of original flux) for about 2 weeks after flocculant addition, returning finally to its original value of 4–5 L/(m^2 h) after 2 more weeks. Membrane resistance increased during reactor operation, showing the development of fouling (not removable by the applied backflush cycles). However, TMP remained low, not exceeding 100 mbar over the entire operation. No sludge was wasted during operation. This produced an increase in total solids concentration from 28 to 34 g TSS/L.

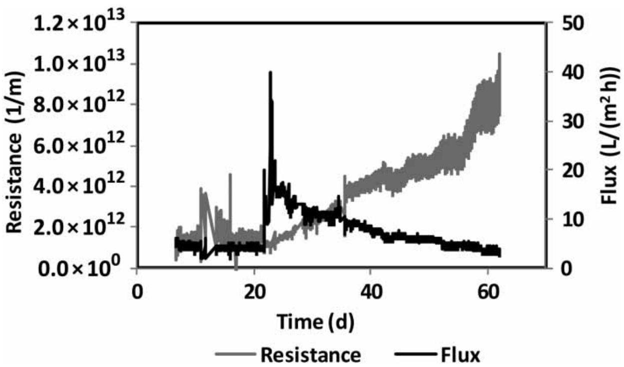

Figure 4 | TMP and permeate flux during the operation of the AnMBR. Flocculant (MPE50) was added on day 22.

Reactor operation shows that MPE50 was successful in enabling flux increase during AnMBR operation, for several days. This is probably the effect of increasing particle size: lower particle deposition due to increase in back-transport, and also lower specific resistance of the formed cake. Indeed, research conducted with aerobic MBRs has shown that fouling-reducing agents such as NALCO MPE can increase cake porosity, reducing resistance and then TMP (Hwang *et al.* 2007). The use of flocculants may be an interesting alternative to cope with unexpected or seasonal increases in inlet flows in AnMBRs, which would require increments in operational flux. Having the possibility to use fouling reducers would enable the reduction of the traditional membrane requirement overestimation, applied indeed to cope with unexpected situations. According to Wozniak (2010), the use of flocculants in aerobic MBRs may reduce investment costs by around 15–20%. No equivalent estimations are available for anaerobic AnMBRs, due to the lack of technical information regarding the flocculants capacity to increase flux. However, it can be calculated that a 100% increase in flux may represent interesting savings in membrane requirement. Doubling the flux would decrease membrane requirements by 50%. If a membrane cost of €50/m^2 and membrane lifetime of 10 years are considered, this decrease in membrane requirements would involve savings equivalent to close to €0.1/m^3 of treated wastewater.

It is not clear if products like the one tested in this research could be applied on a regular basis, nor how they will behave under different conditions, such as different wastewaters and reactor configurations. More research is definitively needed in that direction. However, use of flux-enhancing products seems to be an interesting alternative to cope with unexpected situations, requiring temporary increases in permeate flow.

CONCLUSION

Use of flocculants has been presented previously as a rapid and effective way to increase operational flux in aerobic MBRs dedicated to wastewater treatment. This research confirms that commercial flocculants developed for aerobic

MBRs may be used in anaerobic MBRs to cope with temporal increases in required flux. However, more detailed research is needed with respect to the dynamics of floc disintegration in order to determine the periodicity of flocculant addition.

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