Tracing membrane foulants in membrane bioreactors by filtration characterisation and fractionation

S.P. Geilvoet*, M. Remy, H. Evenblij*, H. Temmink** and J.H.J.M. van der Graaf***

*Department of Water Management, Section for Sanitary Engineering, Delft University of Technology, PO Box 5048, 2600 GA Delft, The Netherlands (E-mail: S.P.*Geilvoet@CiTG.TUDelft.nl*)

**Wetsus, Centre for Sustainable Water Technology, PO Box 1113, 8900 CC Leeuwarden, The Netherlands

Abstract A pilot MBR was fed with two different influent loading conditions, namely dry weather flow (DWF) and DWF with an additional discharge of wastewater from a local cheese factory. For both situations sludge was sampled from different tanks of the pilot (predenitrification, denitrification, nitrification and membrane tank). All sludge samples and the supernatant of sludge from the membrane tank were filtered under exactly the same conditions with a filtration characterisation unit. Besides this all samples were subdivided in different fractions (supernatant, 0.45 and 0.03 μm, 500, 100, 10 and 1 kDa) and analysed for their EPS concentrations (proteins and polysaccharides). The results show that the filterability of the sludge changes with the sampling point and differs between the two influent loading conditions. Contrary to DWF conditions, for cheesy influent conditions sludge from the membrane tank has better filterability than its supernatant. This suggests that the sludge forms a cake layer that protects the membrane against fouling by particles in the free water. No clear relation between filterability and EPS concentrations of the different fractions was found.

Keywords Extracellular polymeric substances; filtration characterisation; fouling; fractionation; membrane bioreactor

Water Science and Technology: Water Supply **Vol 6 No 1 pp 165–172** © IWA Publishing 2006

Introduction

Membrane bioreactor (MBR) technology is considered a promising treatment technology for municipal wastewater. Combining the activated sludge process and membrane separation offers several advantages over the conventional activated sludge process with sludge sedimentation in secondary clarifiers. Most mentioned benefits are the smaller footprint, the superior effluent quality and the possibilities for a flexible and phased extension of existing wastewater treatment plants (Stephenson *et al.*, 2000). Notwithstanding these advantages the widespread application of MBR technology is constrained by the relatively high costs due to the expensive membranes, the relatively high energy consumption and the membrane fouling that takes place during filtration. Membrane fouling is considered to be the most serious problem affecting system performance (Chang *et al.*, 2001; Kim *et al.*, 2001). Periodical cleaning measures are required, leading to an increase of maintenance and operating costs. In recent years much research has been devoted to investigating, modelling and controlling fouling processes. However, because the behaviour of foulants is very complex and depends on various factors, fouling is still a poorly understood process.

Many MBR studies have identified extracellular polymeric substances (EPS) as the most significant biological factor responsible for membrane fouling. EPS is a generic term for a wide range of organic compounds produced by micro-organisms. Among the many functions of EPS are the formation of flocs and a protective layer around the micro-organisms (Wingender *et al.*, 1999). EPS in activated sludge occur in two forms:

doi: 10.2166/ws.2006.020

(1) bound to bacterial cells (extractable EPS); and (2) in the supernatant as slime polymers (suspended EPS). Filterability of activated sludge appears to be particularly influenced by the suspended EPS concentration (Rosenberger and Kraume, 2002).

For research into membrane fouling a filtration characterisation method has been developed, with which the filterability of a given activated sludge sample can be quantified unequivocally. This method was applied for activated sludge samples taken from different zones of a pilot-scale MBR (predenitrification, denitrification, nitrification and membrane tank) treating municipal wastewater and small quantities of wastewater from a local cheese factory. For all sludge samples, as well as for the influent and the supernatant of sludge from the membrane tank, the filtration behaviour was characterised. This was done for two different influent loading conditions, namely for dry weather flow and for dry weather flow with an additional wastewater discharge from the cheese factory. Furthermore, each of the samples was subdivided in several fractions of which the concentration of EPS was determined. The goal of this study consists of two parts: (1) the filterability of activated sludge sampled from different tanks of the pilot is characterised for two different influent loading conditions; and (2) the extent of fouling induced by the sludge samples is correlated to the EPS concentrations in each of the fractions.

Materials and methods

The activated sludge used for the experiments is sampled from a pilot-scale MBR (simulation unit) located at the WWTP of Varsseveld, The Netherlands. The simulation unit has been operational since May 2004 and is equipped with submerged hollow fibre membranes (Zenon ZW500D, nominal pore size 0.04 μm, membrane surface 94.5 m^2, maximum design flow 3.5 m^3/h). The installation has a total tank volume of about 17 m^3 and consists of a predenitrification-, denitrification-, nitrification- and a membrane tank.

On January 13th and 17th of 2005 sludge samples from each of the tanks were collected. Around this period the pilot was constantly operated under dry weather flow conditions.

Firstly on January 13th sludge was sampled at normal conditions, i.e. at dry weather flow (DWF) conditions. Four days later, on January 17th, samples were taken at DWF conditions with an additional discharge of wastewater from a local cheese factory, indicated as cheesy influent (CI) conditions. CI conditions were simulated by adding 1 m^3 of cheese factory wastewater to the DWF influent in a period of 2.5 hours. The addition of cheese factory wastewater took place between 3.5 and 1 hour before sampling.

Filtration characterisation

For research into membrane fouling Delft University of Technology has developed a small-scale filtration installation, schematically represented in Figure 1. The heart of the installation is formed by a single tubular PVDF ultrafiltration membrane module (X-flow F5385, L = 950 mm, D = 8 mm) with a nominal pore size of 0.03 μm.

A peristaltic pump circulates the activated sludge through the system; the cross-flow velocity in the membrane tube is tuned at 1 m/s. Another peristaltic pump is used for permeate extraction; permeate flow rate can be adjusted by tuning the pump speed. The permeate production is measured in time with a mass balance, so the flux J ($L/m^2 * h$) can be calculated. Using three pressure gauges (feed, concentrate and permeate) the transmembrane pressure (TMP) (bar) during an experiment is monitored. The viscosity η (Pa * s) of permeate is assumed to be equal to pure water. From these three parameters the filtration resistance R (m^{-1}) can be calculated according to the following formula:

$$R = TMP/(\eta * J)$$

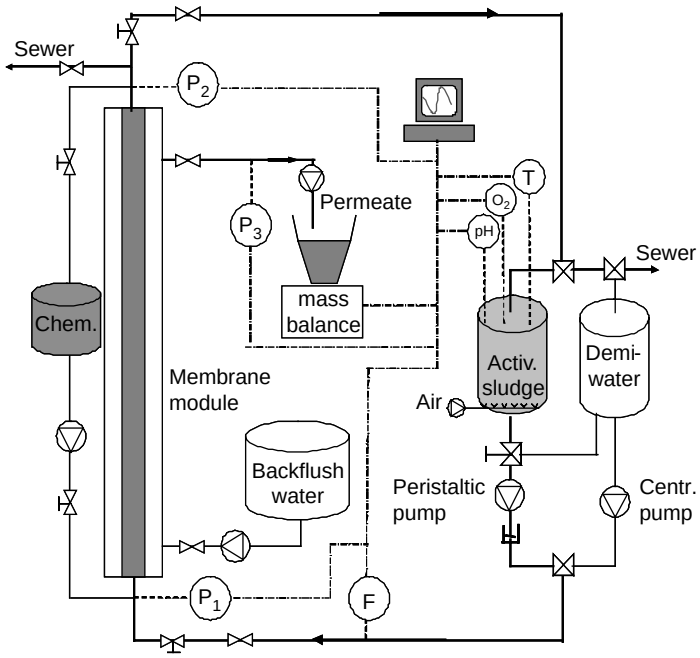

Figure 1 Schematic overview filtration installation

With the filtration installation different activated sludge samples can be filtrated under exactly the same conditions. This enables us to relate differences in filterability directly to differences in sludge quality parameters. Previously, the filtration characterisation method has successfully been applied to show differences in filterability between sludge samples manipulated by substrate addition (Evenblij *et al.*, 2005a) and from different MBR pilots (Evenblij *et al.*, 2005b).

In order to obtain unequivocal results all filtration experiments are conducted following a measuring protocol consisting of three steps:

1. Clean water resistance (CWR) measurement.
   The membrane has to be clean prior to a sludge filtration experiment. To check this demineralised water is filtrated with CFV $=$ 1 m/s and J $=$ 80 L/m^{2}h. For a clean membrane the filtration resistance should be about $0.4 \times 10^{12}\,\mathrm{m}^{-1}$ ($\pm 0.05 \times 10^{12}\,\mathrm{m}^{-1}$). If the CWR is too high supplementary cleaning measures are necessary (see #3).
2. Sludge filtration.
   An activated sludge sample (about 25 litres) is filtrated with CFV $=$ 1 m/s and J $=$ 60 L/m^{2}h for half an hour or until the maximum TMP of 0.75 bar is exceeded.
3. Membrane cleaning.
   After sludge filtration the membrane is cleaned for the next experiment. This can be done by a forward flush (demi-water, 4 m/s), back flush (demi-water, $-$0.75 bar) and chemical cleaning (NaOCl 500 ppm, soaking 15 minutes).

Fractionation

After the samples are collected they are fractionated, according to the schedule outlined in Figure 2. Supernatant is obtained by centrifugation of the sludge samples (3,000 rpm, 11 minutes). The supernatant is further fractionated with a Kubota flat sheet microfiltration membrane ($<$0.45 μm). The finer fractions are prepared with a stirred ultrafiltration

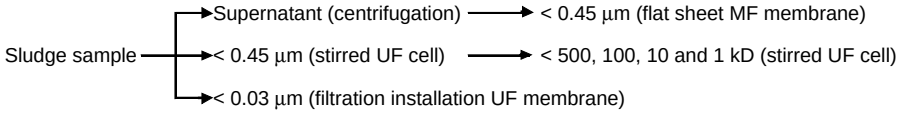

Figure 2 Fractionation schedule

cell (Amicon, model 8050) with hydrophilic cellulose membranes at a pressure of 3 bar. The permeate of the filtration installation represents the $< 0.03\,\mu m$ fraction.

EPS analyses

The analyses discussed in this article are the EPS concentrations in each of the fractions. They are measured as the concentration of their main constituents, proteins and polysaccharides. Protein and polysaccharide concentrations in the free water are measured according to the Bradford method (1976) using Bio-Rad protein assay reagent and to the method of Dubois *et al.* (1956) called the Phenol-H_2SO_4 method.

Results and discussion

Filterability

Figure 3 outlines the filterability of the activated sludge samples per sampling point for the two influent loading conditions, at a flux of $60\,L/m^2 * h$. As a result of the formation of a cake layer the filtration resistance increases quadratically with the produced volume permeate. In the figures the additional resistance is represented as a function of the filtrated volume permeate divided by the membrane surface. Compared to previous experiments with other pilots (Evenblij, 2005b) the sludge can be characterised as "difficult to filter".

Because at CI conditions influent supply was stopped about one hour before sampling no influent could be collected for filtration characterisation. Also no filtration curve was produced for sludge from the denitrification tank due to a computer error.

For DWF conditions the differences between the different sludge samples are quite small. Surprisingly, sludge from the membrane tank has the lowest filterability of all samples. Also the supernatant of the membrane tank sludge causes considerable fouling. This suggests that particularly the suspended particles in the free water are responsible for fouling. Influent has a better filterability than the sludge samples. However, after sludge filtration the membrane could be cleaned with a forward flush, whereas after influent filtration chemical cleaning was required to remove the fouling. This indicates two different fouling mechanisms: for sludge the resistance is caused by the formation of an

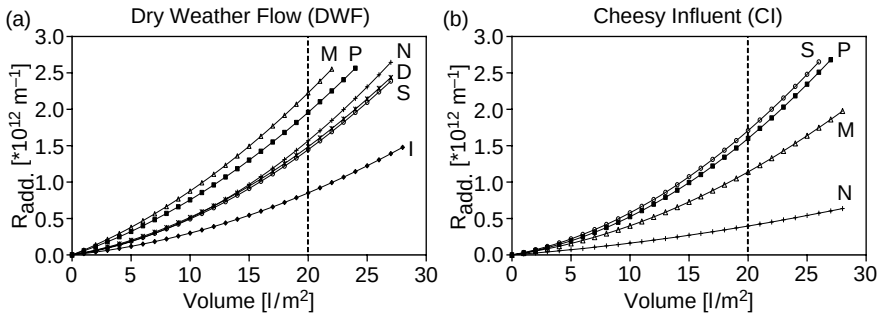

Figure 3 Filtration characteristics for DWF and cheesy influent conditions at $J = 60\,L/m^2 * h$. Key: Influent (I), Predenitrification (P), Denitrification (D), Nitrification (N), Membrane tank (M), Supernatant membrane tank (S)

easily removable cake layer, while for influent filtration particles seem to attach more tightly to the membrane surface.

For CI conditions larger differences in filterability between the sampling points were observed, with the best filterability for sludge from the nitrification tank. The supernatant of the membrane tank sludge has the lowest filterability.

To emphasise the differences between the sampling points and the different influent loading conditions, in Figure 4 the filterability per sampling point is shown as the additional filtration resistance after filtrating a permeate volume of 20 L/m^2 (20 minutes of filtration time).

For both influent loading conditions filterability improves in the nitrification tank compared to the predenitrification tank and then deteriorates again in the membrane tank. As the effluent of the cheese factory has a high concentration of pollutants it was expected that more fouling would occur for CI conditions. However, this is not the case; for all sampling points filterability of sludge is better at CI conditions. Only the filterability of the supernatant is worse for CI conditions compared to DWF conditions.

In particular the differences in filterability of sludge from the membrane tank and its supernatant are remarkable. For DWF conditions the additional resistance at $V = 20\,L/m^2$ is twice as high compared to CI conditions, which demonstrates that the sludge/water mixture at CI conditions has much better filterability. Furthermore the results show that for DWF conditions the supernatant has better filterability than the sludge, while for CI conditions it is the other way around. This indicates that for CI conditions the sludge forms a relatively permeable cake-layer that protects the membrane against fouling by particles in the free water (supernatant).

Free EPS

Figure 5 represents the measured protein concentrations for all sampling points and fractions. For DWF conditions an extremely high protein concentration is found in the supernatant of the influent (200 mg/l). In the first tank of the MBR, the predenitrification tank, the protein concentration is already strongly reduced (116 mg/l). This reduction continues; in the next three tanks concentrations are about 15 mg/l. For the other fractions the differences between the sampling points are smaller. The influent contains the highest concentrations, but for the sludge samples the values are approximately similar. CI conditions show considerable differences compared to DWF conditions. The protein concentration in the supernatant is about two times lower than at DWF conditions (107 mg/l). However, this concentration is maintained throughout most of the process, whereas for DWF conditions protein concentrations are reduced quickly. Furthermore the sludge

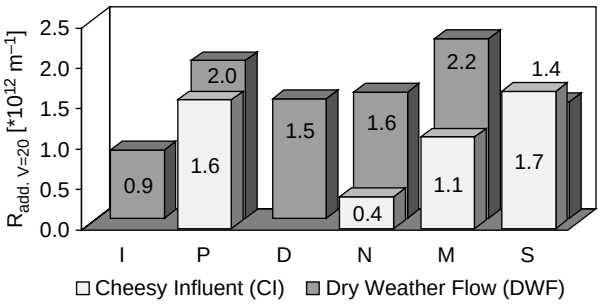

Figure 4 Additional resistance per sample at $V = 20\,L/m^2$ for $J = 60\,L/m^2 * h$. Key: Influent (I), Predenitrification (P), Denitrification (D), Nitrification (N), Membrane tank (M), Supernatant membrane tank (S)

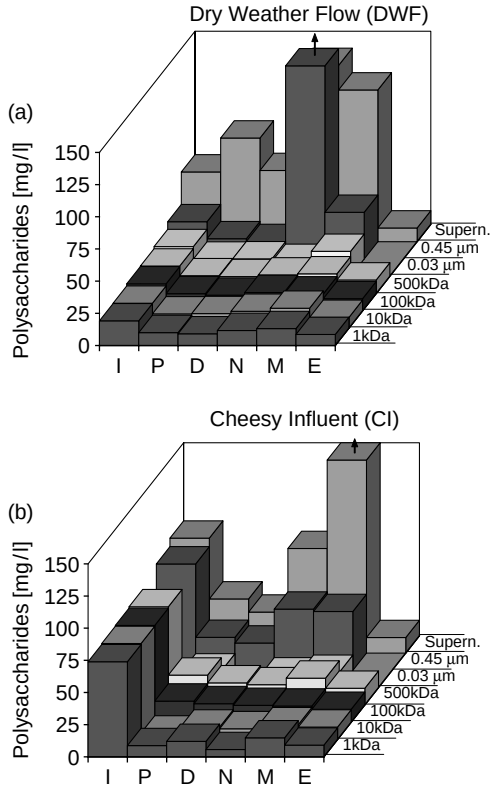

Figure 5 Protein concentrations per sampling point and per fraction. Key: Influent (I), Predenitrification (P), Denitrification (D), Nitrification (N), Membrane tank (M) and Effluent pilot (E)

samples at CI conditions contain a relatively high fraction of proteins smaller than 0.45 μm.

For polysaccharides also significant differences between the different influent loading conditions can be observed; see Figure 6. For DWF conditions the supernatant contains varying polysaccharide concentrations. However, the variations among the sampling points are considerable. For the <0.45 μm fraction an extremely high concentration is found in the nitrification tank (167 mg/l). The reliability of this value is questionable, although also in the membrane tank a relatively high concentration of polysaccharides in the <0.45 μm fraction is found (36 mg/l).

For CI conditions considerable variations in the polysaccharide concentrations of the supernatant are also measured, with by far the highest value in the membrane tank (influent 89 mg/l, predenitrification 42 mg/l, denitrification 32 mg/l, nitrification 81 mg/l, membrane tank 170 mg/l, effluent 12 mg/l). The values measured in the influent are remarkable. For all fractions the measured polysaccharide concentrations are approximately the same. This indicates that all polysaccharide particles are extremely small (<1 kDa).

EPS versus filterability

Both filterability and EPS concentrations in the supernatant differ per sampling point. However, these differences cannot be clearly related to each other. For example, sludge sampled from the nitrification tank at CI conditions relatively has a good filterability (Figure 3), while EPS concentrations are comparable with the other tanks (Figures 5 and 6).

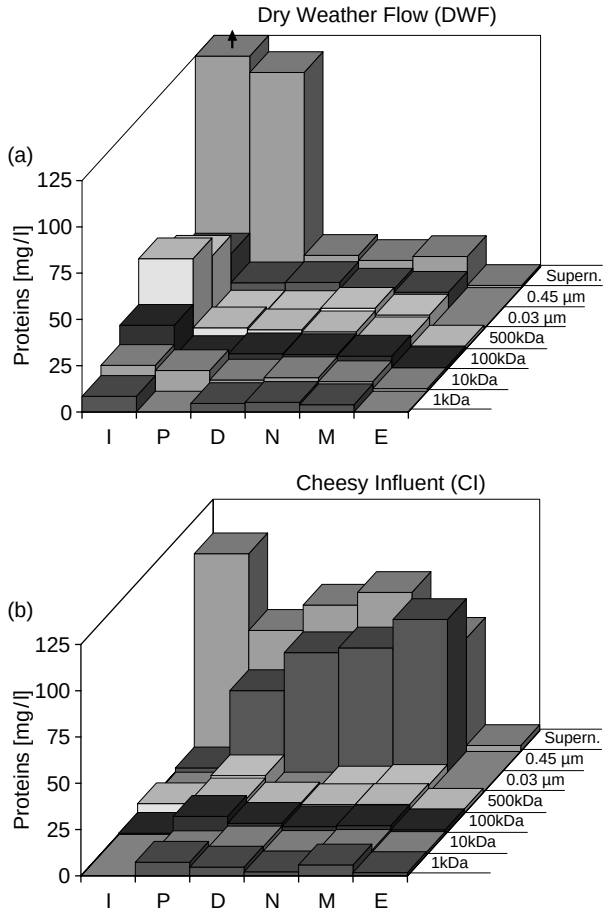

Figure 6 Polysaccharide concentrations per sampling point and per fraction. Key: Influent (I), Predenitrification (P), Denitrification (D), Nitrification (N), Membrane tank (M) and Effluent pilot (E)

This also applies the other way around. For instance, sludge sampled from the predenitrification tank at DWF conditions relatively has a very high protein concentration in the supernatant (Figure 5), but the filterability of the sludge is comparable with the other sampling points (Figure 3).

More information about the relation between EPS concentrations in the free water and the filterability is searched for by comparing the two different influent loading conditions. A remarkable difference between DFW and CI conditions is found in the filterability of sludge from the membrane tank and its supernatant (see Figures 3 and 4) and in the protein concentrations of the supernatant and the $<0.45\,\mu m$ fraction (see Figure 5). These two fractions show much higher protein concentrations at CI conditions than at DWF conditions. With reference to the filterability of the sludge and the supernatant from the membrane tank, these results could indicate that these fractions are responsible for a relatively permeable cake layer that is formed at CI conditions.

Conclusions

The filtration characterisation results show that the filterability of activated sludge changes with the sampling point of the MBR. Especially for cheesy influent conditions the differences are considerable. Sludge sampled from the nitrification tank has by far the

best filterability. Also considerable differences in filterability between the two imposed influent loading conditions appear; the wastewater of the cheese factory contains a high concentration of pollutants, but contrary to expectations the filterability of the sludge is better at CI conditions.

Per sampling point, significant variations in EPS concentrations are only measured in the supernatant. However, these variations cannot be linked with the filterability of the sludge samples. For the smaller fractions EPS concentrations are more or less the same for all sampling points.

Remarkable differences in EPS concentrations between the two influent loading conditions appear. The protein concentration of the $< 0.45\,\mu m$ fraction is higher at CI conditions. It is not clear if, and if so in which way, these differences in EPS concentrations per fraction affect the filterability of the sludge samples.

The experiments have not shown a clear relationship between EPS concentrations in one of the fractions and the filterability of the sludge samples. However, for both influent loading conditions considerable differences in filterability are measured. This forms a good basis for future research. To gain more insight into the mechanisms that cause fouling it is advisable to involve more sludge quality parameters in the research. Besides the EPS concentrations discussed in this article, for example COD, suspended solids and nutrient concentrations, viscosity and particle size distributions can provide more information.

Acknowledgements

The authors would like to thank Waterschap Rijn en IJssel, DHV Water, TNO and X-flow for their financial and practical support and Wageningen University for providing the measuring location.

References

Bradford, M.M. (1976). A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Analytical Biochemistry*, **72**, 248–254.

Chang, I.S., Kim, J.S. and Lee, C.H. (2001). The effects of EPS on membrane fouling in a MBR process. *Proc. MBR3 Conf., Cranfield*, 19–28.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956). Colourimetric method for determination of sugars and related substances. *Analytical Chemistry*, **28**, 350–356.

Evenblij, H., Verrecht, B., Van der Graaf, J.H.J.M. and Van der Bruggen, B. (2005a). Manipulating filterability of MBR activated sludge by pulsed substrate addition. *Desalination*, **178**, 193–201.

Evenblij, H., Geilvoet, S.P., Van der Graaf, J.H.J.M. and Van der Roest, H.F. (2005b). Filtration characterisation for assessing MBR performance: three cases compared. *Desalination*, **178**, 115–124.

Kim, J.S., Lee, C.H. and Chang, I.S. (2001). Effect of pump shear on the performance of a crossflow membrane bioreactor. *Water Research*, **35**, 2137–2144.

Rosenberger, S. and Kraume, M. (2002). Filterability of activated sludge in membrane bioreactors. *Desalination*, **151**, 195–200.

Stephenson, T., Judd, S., Jefferson, B. and Brindle, K. (2000). *Membrane bioreactors for wastewater treatment*, IWA Publishing, London, UK.

Wingender, J., Neu, T.R. and Flemming, H.-C. (1999). *Microbial Extracellular Polymeric Substances – Characterisation, Structure and Function*, Springer, Berlin/Heidelberg/New York, pp. 1–16.