Low concentration of powdered activated carbon decreases fouling in membrane bioreactors

Maxime José Jean Remy

Thesis committee

Thesis supervisor
Prof. dr. ir. W. H. Rulkens
Professor of Environmental Technology
Wageningen University

Thesis co-supervisor
Dr. ir. B. G. Temmink
Assistant professor, Sub-department of Environmental Technology
Wageningen University

Other members
Prof. dr. ir. R. Boom, Wageningen University, the Netherlands
Prof. dr. R. Canziani, Politecnico di Milano, Italy
Prof. dr. ir. I. Nopens, Ghent University, Belgium
Dr. ir. A. J. B. Kemperman, University of Twente, Enschede, the Netherlands

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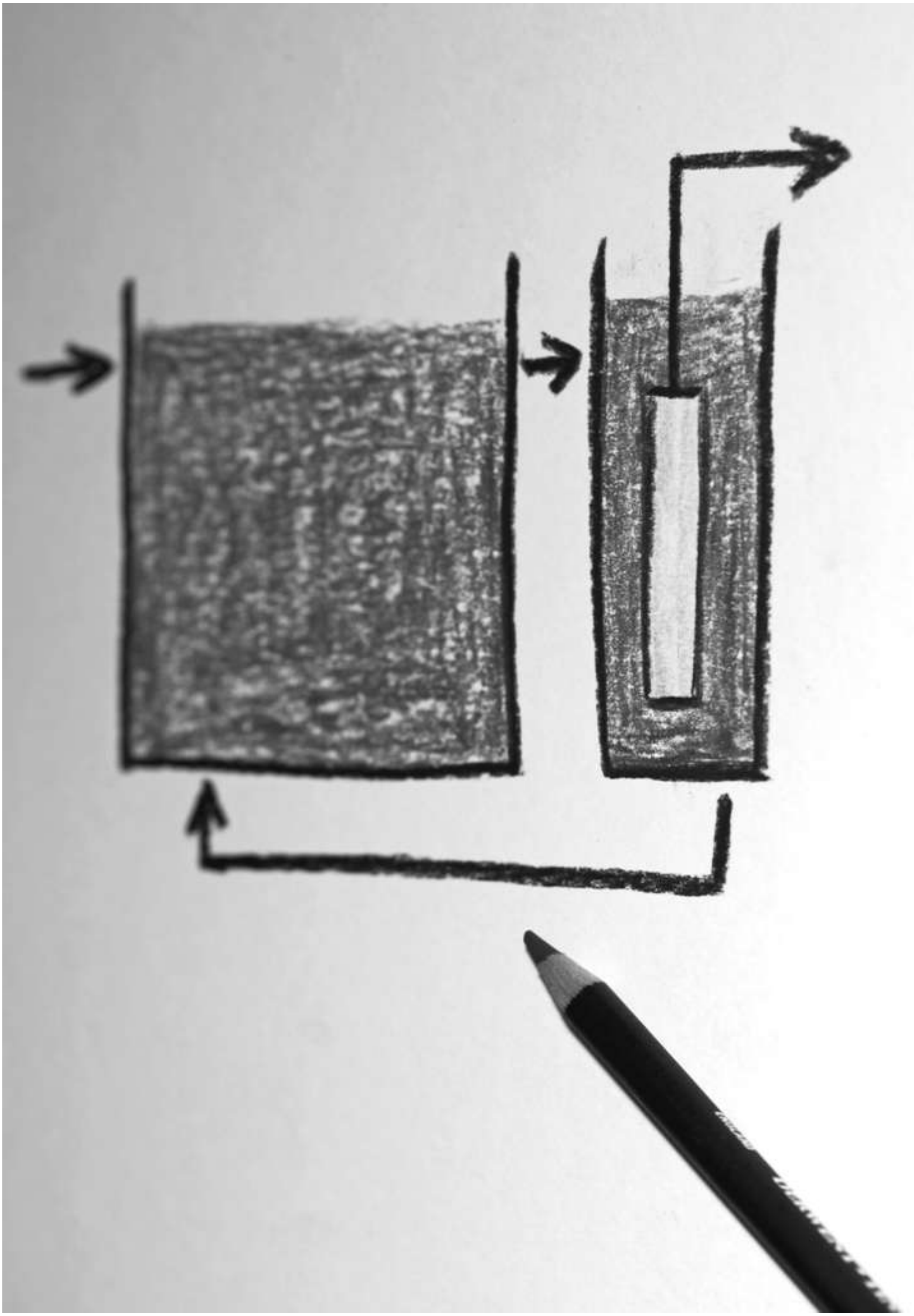
TABLE OF CONTENTS



Chapter 1. GENERAL INTRODUCTION

Abstract - Wastewater treatment became of vital importance over the years, with population growth, to prevent diseases from spreading and limit the impact on the environment. Membrane bioreactors (MBRs) offer several advantages compared to conventional systems employing sedimentation to separate sludge from treated wastewater, including a smaller footprint and an improved effluent quality. Nevertheless, MBRs still encounter several bottlenecks for a more widespread application. They require at least a 30% higher energy input, which only can be minimized by reducing membrane fouling. Factors influencing this fouling are membrane properties, the operation of the MBR and the properties of the feed of the membranes. The latter was selected as the aspect on which this thesis will focus, via modification of the feed characteristics to decrease fouling.

Keywords - wastewater treatment; activated sludge; membrane bioreactor; MBR; membrane fouling.

1.1. Conventional activated sludge systems

Treatment of municipal wastewater is of vital importance for a good functioning of a society. In the past, natural watercourses were used to discharge untreated wastewater. Due to population growth and urbanization, severe detrimental effects for public health happened, such as cholera outbreaks in big cities in the 19th century, making this practice not anymore acceptable. To avoid these dangers, and to protect the environment, sewers were built, initially to collect and transport the dangerous wastewater out of cities and later on to wastewater treatment plants (WWTPs). A combination of mechanical treatment and biological activated sludge treatment is currently the most common way to remove pollutants from the wastewater. Activated sludge consists of settleable sludge flocs containing micro-organisms, responsible for the mineralization of organic pollutants (expressed as chemical oxygen demand or COD) to CO_2 and water (Metcalf & Eddy, 2003). Most municipal WWTPs are so called conventional activated sludge systems (CAS), in which the activated sludge is separated from the treated wastewater by secondary clarification. In this manner the active biomass can be retained in the treatment system. Usually these clarifiers are round basins with a relatively large surface area compared to the bioreactor. Clarification also limits the sludge concentration, also referred to as mixed liquor suspended solids (MLSS) concentration, that can be maintained in the bioreactor, typically to values of 4 to 6 g L^{-1} (Metcalf & Eddy, 2003).

Conventional WWTPs (figure 1) not only consist of a bioreactor and a clarifier. Debris and sand, which can cause problems with pumps and clogging, are often removed from the system before entering the reactor. Primary sludge is removed to lower the loading of the biological reactor. This primary sludge is produced in the primary treatment step that consists of grit removal, flotation, sieving and/or primary sedimentation. To remove the nutrients nitrogen and phosphorus, which otherwise would cause eutrophication in receiving surface waters, the bioreactor often is subdivided in different zones. An anaerobic zone promotes the growth of phosphate accumulating organisms (PAO) which remove phosphate (PO_4^{3-}) by accumulating polyphosphates within their cells. Alternatively, multivalent cations can be added to precipitate phosphate (e.g. Fe^{3+} as $FeCl_3$ to form $FePO_4$). In both cases phosphorus ends up in the excess (waste) sludge which after dewatering and digestion can be incinerated. To remove nitrogen, mainly present as ammonia (NH_4^+) in the wastewater, nitrification takes place in the (aerated) aerobic compartment of the bioreactor. In this process nitrate (NO_3^-) is produced, which in the anoxic compartment is then converted to nitrogen gas (N_2) and in this manner is removed from the wastewater. To meet the guidelines of the European Water Framework Directive, the effluent of a CAS system may need to undergo further treatment. This step is referred to as effluent polishing or tertiary treatment and can consist of sand filters for further reduction of the concentration of N and P in the effluent. Tertiary treatment can also aim at disinfecting the effluent by chlorination, UV or O_3 treatment or even at membrane filtration for particle and pathogen removal. Effluent polishing can produce water that is clean enough to discharge to sensitive surface waters (Hoppe *et al.*, 2004) and, if membranes are applied, the effluent can even be used as process water in industry, leading to costs savings in the consumption of fresh water. Different membrane filtration processes are available to accomplish this, using membranes with different pore sizes. Each leads to different reuse possibilities (e.g. Fane, 1996 and Marcucci *et al.*, 2001). Microfiltration membranes, with a pore size ranging from 1 to 0.1 µm, allow the discharge to surface water. Ultrafiltration membranes, with a pore size ranging from 0.01 to 0.1 µm, can allow reuse as process water. When even cleaner water is required, nanofiltration and/or reverse osmosis membranes, with pore sizes below 10 nm, should be applied.

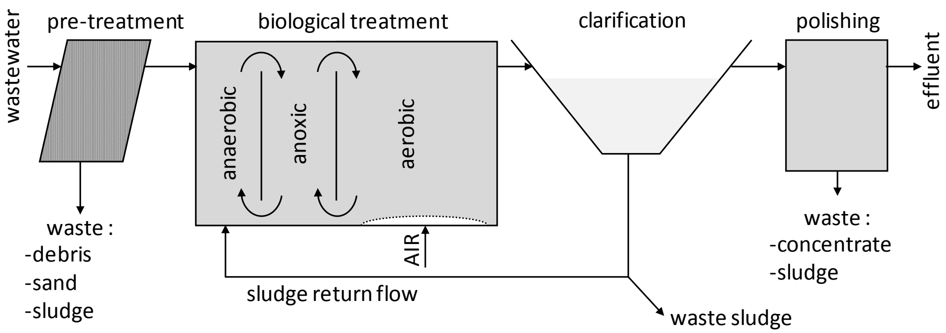


***Figure 1 -** Schematic representation of a municipal WWTP with CAS and effluent polishing.*

1.2. Membrane bioreactors

1.2.1. Membrane bioreactors for wastewater treatment

During the last decade, a tendency can be observed to replace clarifiers by membrane filtration, both micro- and ultrafiltration. The water (permeate) is extracted by a pressure difference, while the activated sludge is retained by the membrane. An important advantage of the membrane bioreactor (MBR), compared to CAS systems is its smaller footprint. Large clarifiers are no longer needed, and it is possible to operate the bioreactors at a higher sludge concentration (typically 10-20 g MLSS L^{-1}), thus allowing smaller biological reactors. In highly populated areas, where land is scarce, this advantage can be particularly decisive for the choice of MBRs over CAS systems. A second important advantage is an improved effluent quality, because the biomass and every component attached to it or with a size bigger than the pore size of the membrane are completely retained in the biological system and removed with the surplus secondary sludge. This implies that regarding particles, the effluent polishing step no longer is required. A third advantage of MBRs is that all the micro-organisms responsible for the treatment process are retained in the system and no longer can be washed out with the effluent. This means that biological treatment becomes feasible, even when the micro-organisms do not aggregate into easily settleable flocs or granules. This would be particularly interesting for industrial applications where e.g. high salinity would prevent formation of settleable flocs. Finally, in MBRs long sludge retention times (SRTs) can be applied, which offers the possibility to maintain high concentrations of specialized, slow growing micro-organisms.

1.2.2. Membrane bioreactor configurations

In MBR systems, membranes can be operated in a side-stream of the biological reactor or can be submerged into the biological reactor (Judd, 2006). For both configurations, finer pre-treatment is necessary to remove hairs that can form bundles in the bioreactors and clog the membranes (Frechen *et al.*, 2007). Side-stream MBRs (Figure 2) are usually based on inside-out filtration through tubular membranes placed outside the bioreactor. The sludge is circulated through the membrane module at high cross flow velocities (up to 5 m s^{-1}) to create the shear that is required to limit fouling of the membranes. Instead of high cross flow velocities, air can be injected to provide the necessary shear and in this manner prevent cake layer deposition (air-lift). In this case, the cross flow velocity by sludge recirculation can be considerably lower (0.3 to 0.5 m s^{-1}). Side-stream MBRs have the advantage of an easier access for cleaning, replacement and maintenance of the membranes. However, they generally require a high energy input (up to 4 kWh m^{-3}), which may account for as much as 60 to 80% of the total energy consumption of MBR operation (Gander *et al.*, 2000).

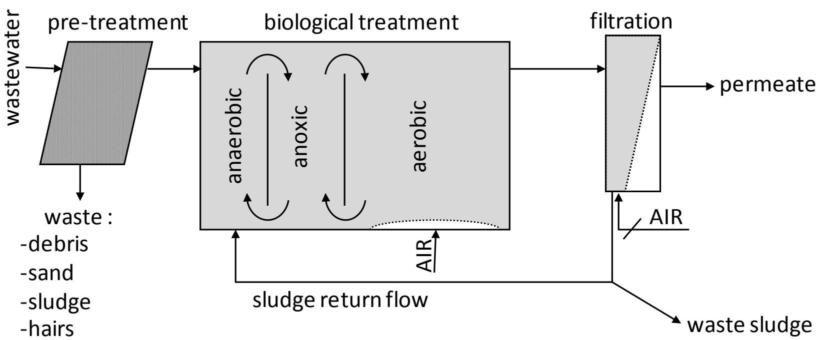


Figure 2 *- Schematic representation of a side-stream MBR.*

The submerged MBR configuration has become increasingly popular because it operates at much lower pressures (0.05 to 0.5 bar) and consumes less energy (0.2 to 0.7 kWh m^{-3}), even though a larger membrane surface area is required as no high membrane flux is possible: (up to 200 L m^{-2} h^{-1} for side stream configurations compared to 20-40 L m^{-2} h^{-1} for submerged configurations), Figure 3 shows a schematic representation of a submerged MBR. The shear at the surface of the membrane to minimize fouling is provided by coarse bubble aeration. In Europe, 99% of the membrane surface area in MBRs is installed in submerged MBRs, of which 75% is applied for treatment of municipal wastewater (Lesjean & Huisjes, 2007). Membranes in submerged MBR can be flat-sheet or hollow fibers applying outside-in filtration. For research, flat sheet submerged membranes are more often selected as they are easier to operate (Le Clech *et al.*, 2005 and Judd, 2006) and allow investigation of the membrane surface.

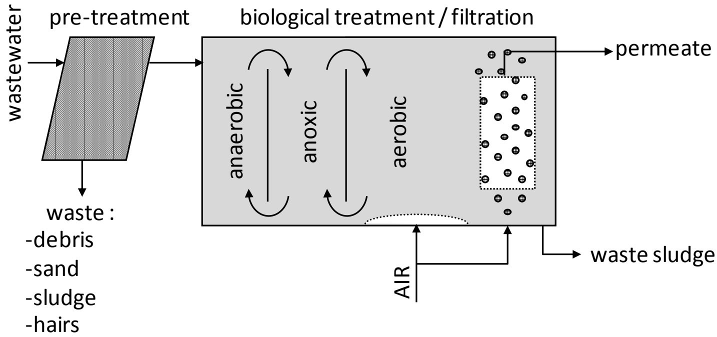


Figure 3 - *Schematic representation of a submerged MBR.*

1.2.3. Bottlenecks for the application of membrane bioreactors

From the above, it could be expected that MBRs are at least a competitive alternative for CAS systems employing clarifiers. Both for municipal and industrial wastewater several full-scale membrane bioreactor applications have been installed. Although the installation costs are comparable to CAS systems with effluent polishing (Adham *et al.*, 2001), one still is rather reluctant to apply MBR technology. They have a reputation to be less robust and require a more complex operation. However, the main reason is that the operational costs of membrane bioreactors are higher than for conventional systems because they consume more energy: e.g. 30% more when compared to a CAS WWTP expanded by sand filtration (Van Bentem & Van der Roest, 2007). Membrane fouling severely limits the membrane flux and necessitates a relatively large membrane area and frequent cleaning (Le-Clech *et al.*, 2006 and Meng *et al.*, 2009). In addition, due to a higher sludge concentration, oxygen transfer is limited, further increasing the energy consumption due to more intensive aeration required (Brouwer *et al.*, 2005 and Germain *et al.*, 2005).

Several solutions for fouling have been proposed, such as back-washing, periodic relaxation, operation at sub-critical fluxes, the introduction of shear forces at the membrane surface (Ng *et al.*, 2005), and cleaning with acids, caustic soda, or sodium hypochlorite, but all of these increase the operational costs and energy consumption. Preventing fouling formation would make the MBR more competitive against CAS.

1.3. Fouling

1.3.1. Fouling mechanisms

Several definitions are given for fouling in the literature. The definition given by Koros *et al.* (1996), formulated by the international union of pure applied chemistry (IUAPC), is: "*Fouling is the process resulting in the loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surface, at its pore openings or within the pores*". This definition later was condensed by Judd (2006) as follows: "*Process leading to deterioration of flux due to surface or internal blockage of the membrane*". In the definition by the IUAPC, membrane fouling can be segregated into different fouling mechanisms (Van den Berg & Smolders, 1990), each causing a certain resistance to filtration:

$$R_{total} = R_m + R_{pb} + R_a + R_{cl} + R_{cp} \tag{1}$$

Each of these resistance mechanisms contributes to a total resistance (R_{total}) during membrane filtration. Figure 4 gives a schematic representation of membrane fouling in MBRs. The membrane resistance (R_m) is inherent to the membrane and can be measured by filtering water without foulants (demineralized water). Pore blocking (R_{pb}) is the resistance caused by substances and particles accumulating in the pores of the membrane, thus blocking it totally. Adsorption (R_a) of substances at the membrane surface or within the pores, results in pore narrowing, thus decreasing the pore size. Cake layer formation (R_{cl}) is a deposition of particulate materials such as sludge flocs and extracellular polymers, generally larger in size than the membrane pores, on the surface of the membrane. Scouring by coarse bubble aeration minimizes the deposition of a cake layers in submerged MBRs. Concentration polarization (R_{cp}) is defined by IUPAC as: "*A concentration profile that has a higher level of solute nearest to the upstream membrane surface compared with the more or less well mixed bulk fluid far from the membrane surface*". This mechanism is important in reverse osmosis membranes applications but is negligible in MBR processes employing micro- or ultrafiltration (Evenblij, 2006 and Koros *et al.*, 1996).

Alternatively, the resistance to membrane filtration can be segregated into reversible and irreversible fouling (Van der Marel, 2009 and Defrance & Jaffrin, 1999) (equation 2).

$$R_{total} = R_m + R_{reversible} + R_{irreversible} \tag{2}$$

Reversible fouling ($R_{reversible}$) is partially prevented by air scouring and can be removed by physical cleaning (Ng *et al.*, 2005), e.g. relaxation (ceasing filtration) or backwashing (reversing of permeate flow). $R_{reversible}$ is similar to R_{cl}, and consists of the deposition of a cake and/or gel layer on the membrane surface. When backwashing is applied, pore blocking (R_{pb}) can also be partly counteracted. It is then to some extent included in the reversible fouling. Irreversible fouling ($R_{irreversible}$) cannot be removed during relaxation and/or backwashing and needs more rigorous chemical cleaning (Liu *et al.*, 2009), by sodium-hypochlorite for organic foulants and/or acids for inorganic fouling (Judd, 2006).

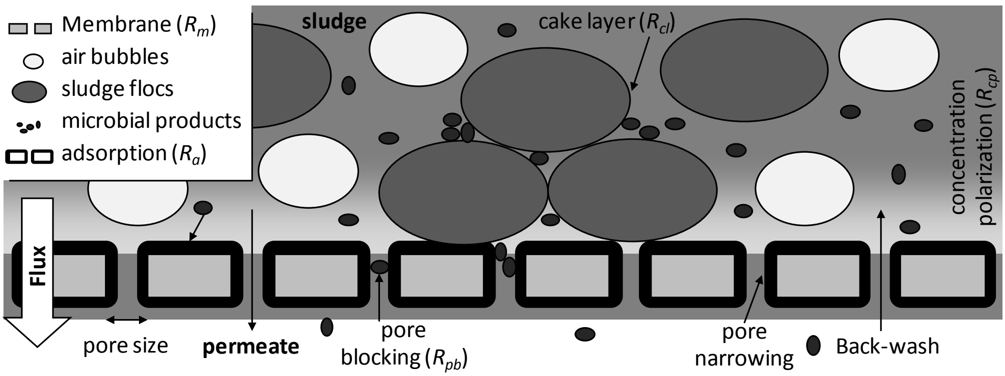


***Figure 4** - Schematic representation of membrane fouling with the different mechanisms.*

When investigating influence of feed properties, fouling refers to the loss of filterability caused by the total resistance $R_{fouling}$ presented in equation 3.

$$R_{fouling} = R_{total} - R_m \tag{3}$$

No distinction is made between the different fouling mechanisms as they are all interrelated and are difficult to present in series as in equation 1. R_m is not taken into account as it is inherent to the system, even though different membrane characteristics can cause the membrane to be more sensitive to certain type of fouling (e.g. pore size and particle size for pore blocking).

1.3.2. Factors affecting fouling

Fouling in MBRs can be influenced by a multitude of factors. In Table 1 these are separated into three main ones: membrane properties, operational conditions and feed/biomass properties (Chang *et al.*, 2002, Le-Clech *et al.*, 2006 and Meng *et al.*, 2009).

Membrane properties	Operational conditions	Feed properties
Membrane material	Flux	Particle size distribution
Roughness	Membrane configuration	Exocellular Polymers
Hydrophobicity and charge	Shear	MLSS concentration
Pore size and porosity	Cleaning procedure	Wastewater composition
Pore morphology	SRT and HRT	Temperature and viscosity

Table 1 - *Factors affecting fouling.*

Membranes can differ in material, pore size distribution, etc. All those properties have an effect on the membrane resistance as well as on their fouling propensity. Van der Marel (2009) presented an extensive study of the influence of membrane properties on fouling. The best performing membrane was a homemade hydrophilic PVDF membrane with an asymmetric interconnected pore structure and a pore size of 0.03 µm. Membrane operation is also determining the fouling potential (e.g. Ng *et al.*, 2005 and Van der Marel, 2009). The membrane flux is commonly chosen to keep fouling at an acceptable level, i.e. low enough to minimize transport of foulants towards the membrane surface. This flux is then below the so-called "critical flux", a concept which was introduced by Field *et al.* (1995). Shear is continuously exerted on the surface of the membrane to back-transport the foulants from the membrane surface with a predilection for those with a large particle size. This can be achieved by cross-flow of the sludge in side-stream MBRs or by coarse bubble aeration in submerged MBRs. Periodic physical cleaning (e.g. back-flushing: Van der Marel, 2009) allow the reactor to run sustainably at a higher flux than without physical cleaning.

Because in MBRs the hydraulic and sludge retention time (respectively HRT and SRT) are uncoupled, MBRs can theoretically be operated at a longer SRT compared to CAS systems. A beneficial effect of a longer SRT with respect to fouling was presented by Nuengjammong *et al.* (2005) and Innocenti *et al.* (2002). Ng *et al.* (2006) related this positive effect of a longer SRT to lower concentrations of free extracellular polymers. However, Lee *et al.* (2003) and Kimura *et al.* (2009) found an opposite effect with more extensive fouling resistance at longer SRTs. Another operational parameter affecting fouling is the concentration of dissolved oxygen (DO) with less fouling at higher DO values (Jin *et al.*, 2006). The temperature (T°) of the feed, although it cannot be controlled, also affects the fouling, with more severe fouling at lower temperatures (Jiang *et al.*, 2005 and Van den Brink *et al.*, 2011).

The characteristics of the sludge that is fed to the membrane are also of highly importance for a good operation of MBRs, although these characteristics are determined by the operational conditions and the wastewater characteristics (figure 5). Research has been focused mostly on membrane operation and module design (Le Clech *et al.*, 2006). Literature data on the effect of feed characteristics and the origin and nature of the foulants is conflicting (Drews, 2010). Besides a higher MLSS, MBRs are still operated in a similar way as CAS with respect to the biological process.

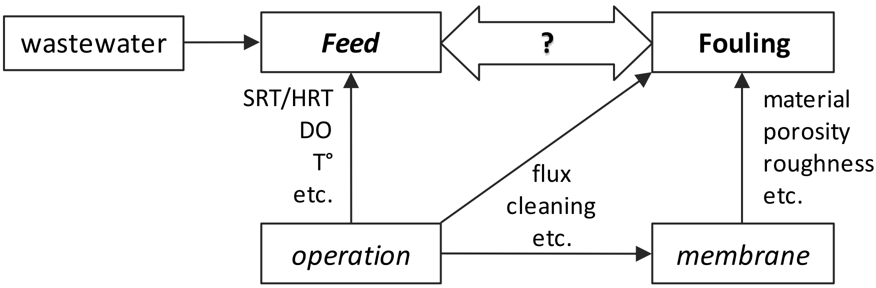


Figure 5 *- Schematic representation of factors affecting fouling.*

1.4. Objective and outline of the thesis

The objective of this thesis is to investigate the possibilities to decrease membrane fouling in MBRs by optimizing the feed characteristics. Emphasis is set on flocculation and floc strength which are considered of prime importance for sludge filterability. Dosing of powdered activated carbon (PAC) as an additive to activated sludge is selected to decrease fouling. Attention is also given to the effect of dosing on sludge properties as well as on the robustness of a MBR under adverse conditions.

Chapter 2 of this thesis describes the results of an extensive monitoring session during the start-up of the first Dutch full-scale MBR in Varsseveld (STOWA, 2006). Several sludge properties were followed in time, along with the fouling potential of the sludge to be able to identify the most important sludge properties involved in membrane fouling. Flocculation and floc strength showed a strong correlation with fouling. In **chapter 3**, the findings of the monitoring session presented in chapter 2 were verified in the laboratory through shear tests. A literature review was conducted to select possible methods to improve flocculation; hereby decreasing fouling in MBRs. Addition of powdered activated carbon (PAC) to MBRs was further investigated. **Chapter 4** describes a pilot-scale study of the effect of PAC addition on the long term filterability of sludge and the critical flux. Measurements were conducted with the sludge from two pilot-scale MBRs running in parallel, one of which was amended with a low dose of PAC. **Chapter 5** describes a study of the mechanisms causing the positive effect of PAC. Literature on PAC addition actually proposes different mechanisms: an improved scouring of the cake layer on the membrane surface, adsorption of foulants, and increased floc strength. The contribution of each one of those mechanisms was assessed individually via experiments. **Chapter 6** shows the long-term (more than a year) effect of PAC addition in a pilot scale MBR running on municipal wastewater. Membrane fouling, oxygen transfer, effluent quality and sludge dewaterability were investigated. **Chapter 7** deals with a study on the effect of PAC addition to counteract conditions known to be unfavorable for sludge filterability, i.e. an increased concentration of monovalent ions and lower temperature. The main conclusions and findings of the thesis are summarized in **chapter 8.** Also an estimation of the economic effect of PAC addition for a full-scale MBR is given. A possible optimization for further cost reduction is elaborated and recommendations for future research are discussed.

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Chapter 2. RELATION BETWEEN SLUDGE QUALITY AND FILTERABILITY DURING START-UP OF A FULL-SCALE MEMBRANE BIOREACTOR

Maxime Remy[1,2], Hardy Temmink[1,2] and Stefan Geilvoet[3]

[1.] Wetsus, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

[2.] Wageningen University, Sub-department of Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

[3.] Delft University of Technology, Faculty of Civil Engineering and Geosciences, Stevinweg 1, 2628 CN Delft, The Netherlands

Abstract - Membrane fouling is an important bottleneck for the application of membrane bioreactors. The sludge quality with respect to filterability is one of the factors determining this fouling. Therefore the relation between sludge quality and filterability was investigated for almost a year during the start-up of a full-scale membrane bioreactor. The results verified a strong relationship between filterability and sludge quality, in particular between filterability and hydrophobicity, the concentration of polysaccharides in the colloidal fraction of the sludge, and the organic fraction of the sludge. These observations strongly indicate that flocculation is the key mechanism determining membrane fouling and that future research to reduce this fouling should focus to maintain the concentration of colloidal matter in the sludge mixture as low as possible.

Keywords: membrane bioreactor; MBR; membrane fouling; activated sludge; sludge quality; filterability

adapted from:

STOWA (2006), MBR rapport Varsseveld, STOWA report number 2006-05 and 2006-06.

Temmink, B. G., Remy, M. J. J. and Geilvoet, S. (2007), Relatie tusen filtreerbaarheid en eigenschappen van het slib-water mengsel uit de full-scale MBR in Varsseveld, Afvalwaterwetenschap 6 (1), pp. 14-25.

2.1. Introduction

Membrane fouling probably is the most important bottleneck for a wide-spread application of membrane bioreactors (MBRs) because it results in: (1) a lower design flux and herewith a larger and more expensive installed membrane surface area, (2) a higher energy consumption associated with (mechanical) membrane cleaning to avoid deposition of and/or remove reversible fouling from the membrane surface and (3) more frequent chemical cleaning to remove irreversible fouling.

Membrane fouling in MBRs is a very complex phenomenon determined by the composition and properties of the feed sludge, membrane properties (membrane material, pore size and morphology, etc.) and membrane operation (Chang *et al.*, 2002). This chapter focuses on the relation between sludge properties and sludge filterability. Figure 1 presents a simplified picture of a sludge floc and its environment. It consists of an agglomerate of different active and dead micro-organisms and mineral particles, held together by polymers which are excreted by the active micro-organisms. These polymers, in literature usually referred to as extracellular polymeric substances (EPS), can be polysaccharides, proteins, nucleic acids and humic like compounds. Multivalent cations such as Ca^{2+}, Mg^{2+} and Fe^{3+} have a crucial role in that they provide bridges between the polymers. The bulk water contains dissolved substances, which originate from the wastewater or are excreted by the micro-organisms, free EPS, and colloidal matter, mostly consisting of fine floc fragments. Even this simplified picture already shows that multiple sludge properties are involved in membrane fouling. The solids concentration, floc size, floc strength, the presence of multivalent cations, the concentration and composition of EPS and of the colloidal matter all are important parameters. In addition, these parameters exert a strong and complex interaction.

In this study the relation between several sludge properties and sludge filterability was studied with samples taken from a full-scale municipal MBR. Filterability was determined in a separate set-up to exclude the effect of variable membrane operation. Sufficient variation in sludge properties was obtained by taking samples during the 11 months start-up period of the full-scale MBR.

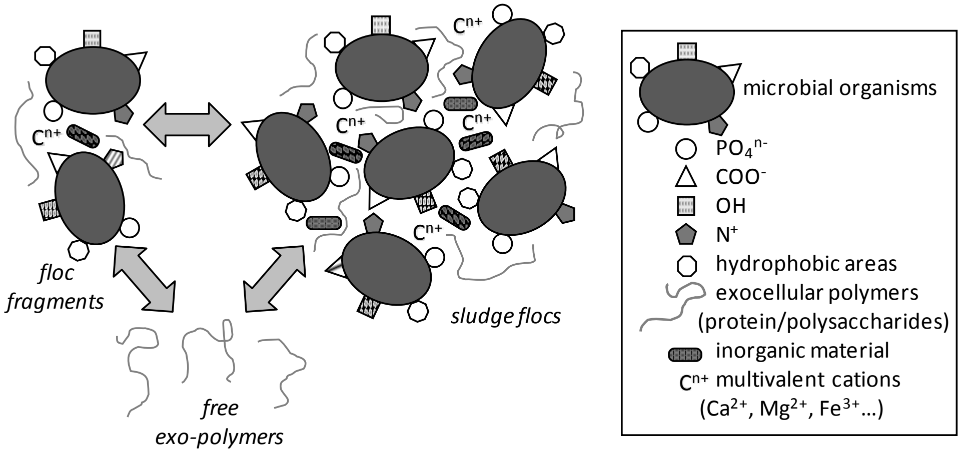

***Figure 1** - Schematic representation of a sludge floc and its environment (adapted from Urbain et al., 1993).*

2.2. Material and methods

2.2.1. Full-scale MBR

Samples were taken from the full-scale MBR of the city of Varsseveld, The Netherlands. This MBR has a design capacity of 23 150 population equivalents, and treats an average and maximum flow rate respectively of 5000 $m^3\ d^{-1}$ and 755 $m^3\ h^{-1}$. The biological reactor, which was inoculated with 8 $g\ L^{-1}$ of sludge from the former activated sludge plant, consists of a pre-denitrification tank, a Carrousel system for nitrification and denitrification, and a separate membrane tank equipped with Zenon Zeeweed 500 membranes (nominal pore size 0.02 µm). The MBR treats municipal wastewater, but during the first 5 months (January-May) of the start-up period in 2005 also treated wastewater from a cheese factory. This wastewater later on was uncoupled because evidence that it contained a polymer causing severe membrane fouling was available. After approximately 6 months, ferric chloride addition was initiated to improve phosphorus removal as biological phosphorus removal was not sufficient to meet the effluent demands.

2.2.2. Filterability

Resistances of clean water, wastewater, sludge and fractions of this sludge were determined in a small-scale membrane set-up, described in detail by Geilvoet *et al.* (2006). The cross-flow velocity in the X-flow tubular inside-out membrane (diameter 8 mm, nominal pore size 0.03 µm, surface 0.024 m^2) was 1.0 m s^{-1}. All samples were filtered at a flux of 60 L m^{-2} h^{-1}. This flux is considerably higher than fluxes of 10-30 L m^{-2} h^{-1} applied in practice to allow fouling to take place. The additional resistance (above the membrane resistance) after the production of 10 L m^{-2} of permeate (R_{add_10}) was selected as an indication of filterability.

2.2.3. Fractionation

Sludge samples from the pre-denitrification tank, nitrification zone of the Carrousel and from the membrane tank of the full-scale MBR were fractionated. Supernatant was obtained by 11 minutes centrifugation at 3000 rpm and subsequent paper filtration (S&S, ME 25/21 STL). Part of the filtrate was further treated in a 0.45 µm submerged flat-plate membrane to obtain a permeate only containing the dissolved fraction of the supernatant.

2.2.4. Sludge quality

EPS, bound to the sludge flocs, was determined according to a method by Frølund *et al.* (1996) and based on extraction with a cation-exchange resin. Total suspended solids (TSS) and volatile suspended solids (VSS) of sludge samples were determined according to standard methods (APHA-AWWA-WEF, 1998). The concentration of proteins in the extracts was measured with a Bio-Rad essay based on the method proposed by Bradford (1976) with immunoglobulin as a standard. Concentrations of polysaccharides in the extracts were determined according to a method given by Dubois *et al.* (1956) with glucose as the standard. Hydrophobicity of the sludge was measured with the MATH test (microbial adsorption to hydrocarbon), described by Guellil *et al.* (1998). Particle size distribution of sludge and wastewater samples was determined on a Coulter Laser model LS 230 equipped with a Fraunhofer optical model.

2.3. Results

2.3.1. Filterability

Figure 2 shows filtration curves of sludge samples taken from the membrane tank of the full-scale MBR during the start-up period. With the exception of the sample taken on February 14th when the permeate extraction was stopped for 7 hours prior to sampling due to an operational failure, a clear distinction can be made between samples taken during the period January-April and samples taken in June and October. Sludge samples taken from January to April exhibited a fast increase in resistance and the filterability was qualified as "poor". Sludge samples from June and October showed a much slower increase of resistance and their filterability was qualified as "good". This trend was also confirmed by observations of the permeability of the membranes in the full-scale MBR, which is described in more detail by Geilvoet *et al.* (2006).

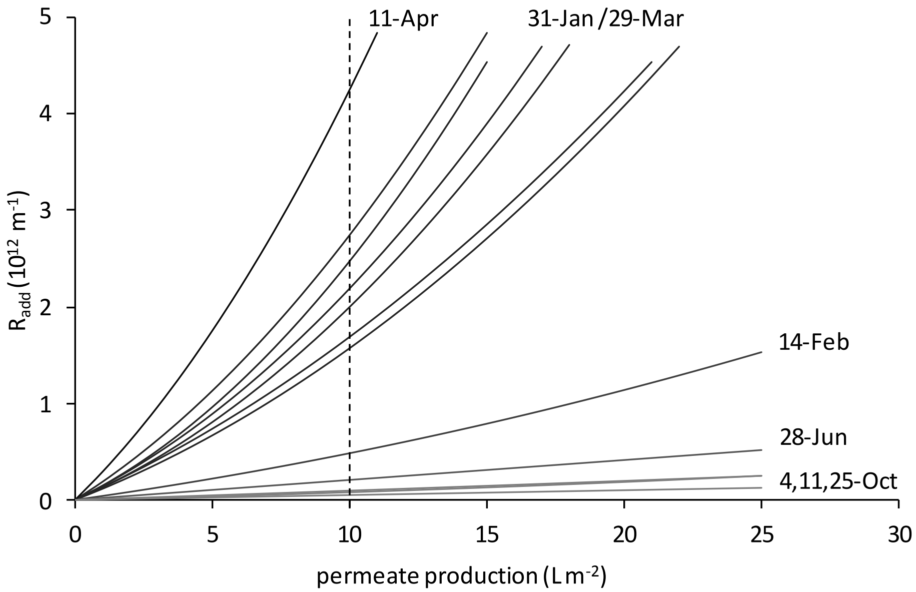

Figure 2 - *Filtration curves of sludge samples taken from the membrane tank of the full-scale MBR.*

The effect of the biological treatment process on sludge filterability was investigated by comparing R_{add_10} values of wastewater and of sludge samples taken from the pre-denitrification tank, nitrification zone of the carrousel and from the membrane tank. Figure 3 shows the most important results. Only two measurements were carried out with sludge from the pre-denitrification tank because sampling was difficult due to the presence of a thick and viscous foam layer on top of the tank (results not shown in Figure 3). The results that were available however indicated a similar filterability as the sludge from the nitrification zone. Filterability of sludge from the membrane tank generally was better than filterability of sludge from the nitrification zone in the carrousel. Low R_{add_10} values obtained with wastewater indicated a good filterability, with the exception of the sample taken on February 28th. Remarkably, during the period January-April the filterability of the sludge was much worse than the filterability of the wastewater, but they were similar in June and October. On October 4th the filterability of sludge was even better than the filterability of the wastewater.

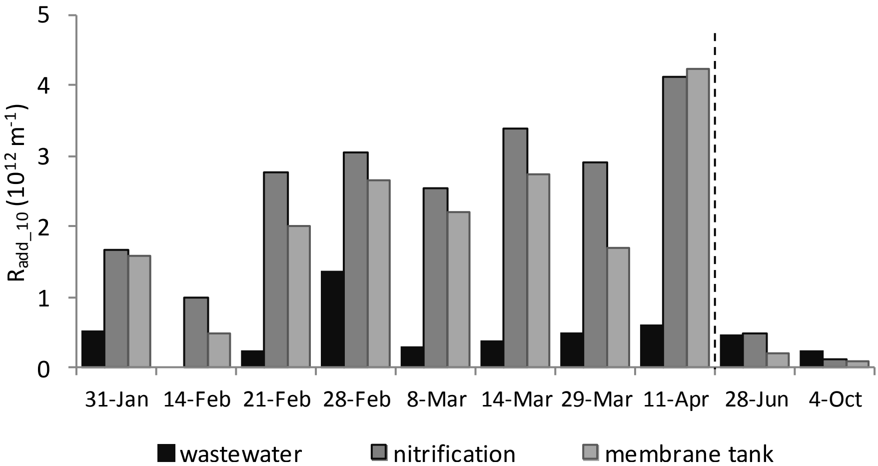

Figure 3 - *R_{add_10} of sludge samples from the nitrification zone and from the membrane tank of the full-scale MBR and of the wastewater.*

Values for R_{add_10} of sludge in the membrane tank, supernatant of this sludge and of 0.45 µm filtered supernatant are shown in Figure 4. Unfortunately the R_{add_10} of the 0.45 µm fraction was not determined on all occasions. A correlation between filterability of the sludge and its supernatant could not be detected. On all occasions the filterability of the supernatant was relatively high, and sometimes larger and sometimes lower than the filterability of the sludge. This indicates that the most important resistance against filtration probably is caused by the supernatant and not by the sludge flocs.

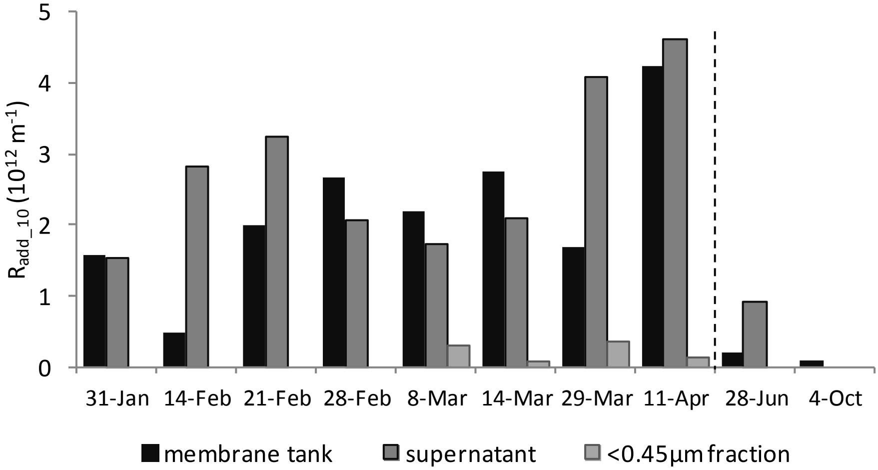

Figure 4 - *R_{add_10} of sludge samples from the membrane tank of the full-scale MBR and supernatant and 0.45 µm filtered supernatant fractions of these samples.*

Also notice that the filterability of the supernatant was much worse than the filterability of the wastewater (Figure 3). This implies that the most important contribution to the additional resistance caused by fouling was not due to wastewater components but by components produced by the micro-organisms. This can be further specified because the filterability of the 0.45 µm filtered fraction of the supernatant always was much better than the filterability of the supernatant itself (Figure 4), indicating that the most of the fouling was caused by supernatant particles in the > 0.45 µm range, i.e. in the colloidal range.

2.3.2. Relation between filterability and sludge quality

The sludge concentration of the samples varied between 8 and 16 g L^{-1}. A clear correlation between sludge concentration and filterability however was absent (data not shown). Figure 5 shows that a correlation between the organic fraction of the sludge and filterability did exist: an increase of the organic content of the sludge from 60 to 80% matched with a strong deterioration of filterability. Sludge samples taken in June and October had a much lower organic fraction than the samples taken from January to April, probably caused by the addition of ferric chloride which started by the end of May causing a "dilution" of the organic fraction with inorganic iron phosphate precipitates.

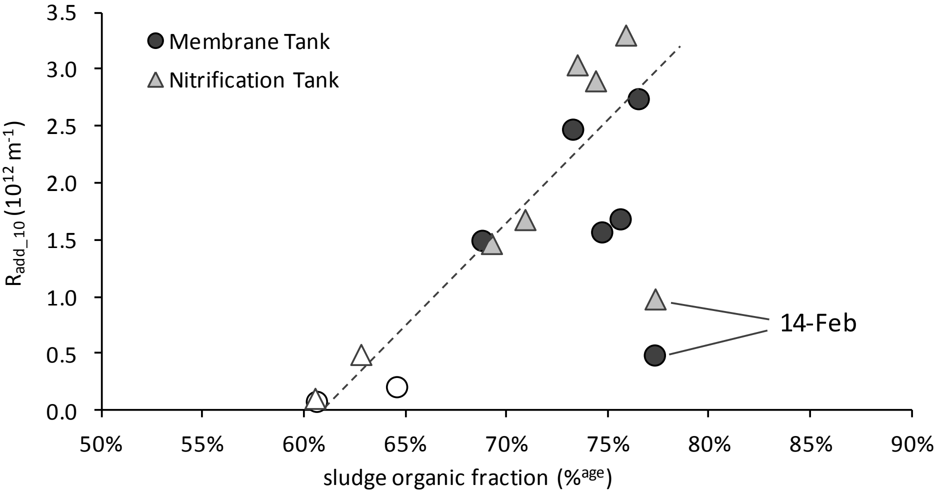

***Figure 5 -** Relation between the organic fraction of the sludge and R_{add_10} (filled data points represent sludge samples from January-April and empty data points represent samples from June and October).*

COD, polysaccharide and protein concentrations in the supernatant of the sludge samples respectively varied from 40-250 mg L^{-1}, 10-100 mg L^{-1} and 10-50 mg L^{-1}, with much higher concentrations in the period before June. COD concentrations in the supernatant were 2-10 times higher than in the permeate, which clearly shows the contribution of membrane retention to overall COD removal. In contrast to proteins, for COD and polysaccharides a clear correlation could be shown with sludge filterability. As an example, Figure 6 shows the relation between the concentration of polysaccharides in the supernatant and R_{add_10}. Lower polysaccharide concentrations result in a lower R_{add_10}, i.e. a better filterability. Also the concentrations of COD, polysaccharides and proteins in 0.45 µm filtered supernatant were determined; although their contribution to the total concentrations in the supernatant were significant (44% for COD, 43% for polysaccharides and 33% for proteins), a correlation with sludge filterability could not be detected.

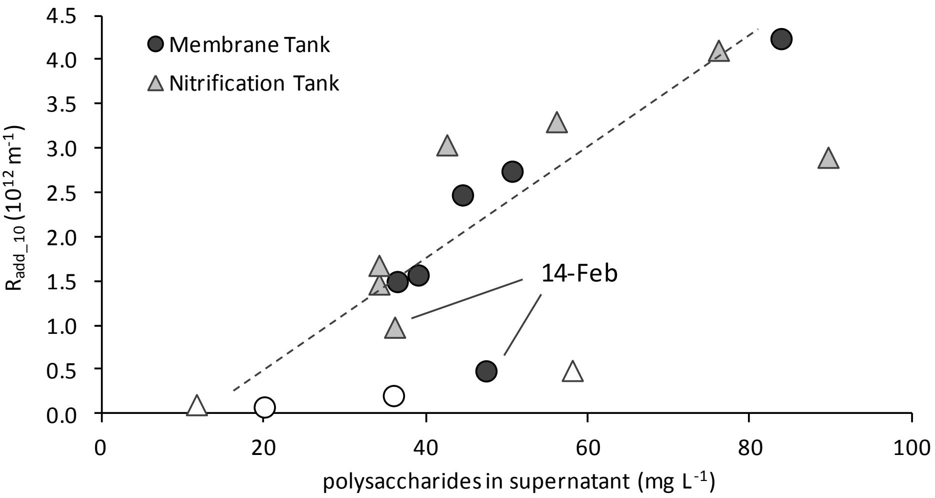

Figure 6 - *Relation between the polysaccharide in the supernatant and R_{add_10} (filled data points represent sludge samples from January-April and empty data point represent samples from June and October).*

Concentrations of extractable EPS in sludge samples varied between 60-180 mg g^{-1} for COD, 15-45 mg g^{-1} for polysaccharides and 4-40 mg g^{-1} for proteins. Similar to the supernatant fraction, the concentrations of extractable EPS were much higher in the period January-April than in June and October.

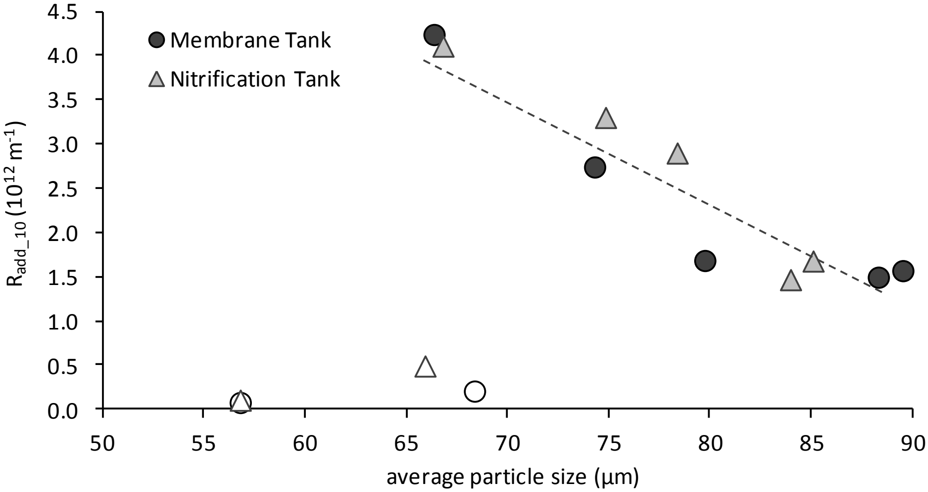

Figure 7 - *Relation between average particle size of the sludge and R_{add_10} (filled data points represent sludge samples from January-April and empty data point represent samples from June and October).*

Figure 7 shows the relation between the average particle size and R_{add_10} of the sludge samples. Again, a clear distinction can be made between samples taken in the period January-April and samples taken in June and October. In January-April the average particle size varied between 65 and 85 µm. In spite of this relatively narrow range, a strong correlation with R_{add_10} can be observed with better filterability (lower values for R_{add_10}) for larger particle sizes. This corresponds with literature information claiming that bigger particles are more easily back transported from the membrane surface than smaller particles. However, In June and October the average particle size was even smaller, between 55 and 65 µm, while filterability was considerably better. Microscopic inspection showed that the sludge flocs in June and October were much more compact than the more fluffy flocs in January-April. Apparently not only the particle size, but mostly the structure of the flocs is important with respect to filterability.

Finally, Figure 8 shows the relation between hydrophobicity, measured with the MATH method, and R_{add_10}. A higher degree of hydrophobicity correlated with a lower R_{add_10}, i.e. a better filterability of the sludge. Hydrophobicity varied between 30 and 80% and was highest for the sludge samples taken in June and October.

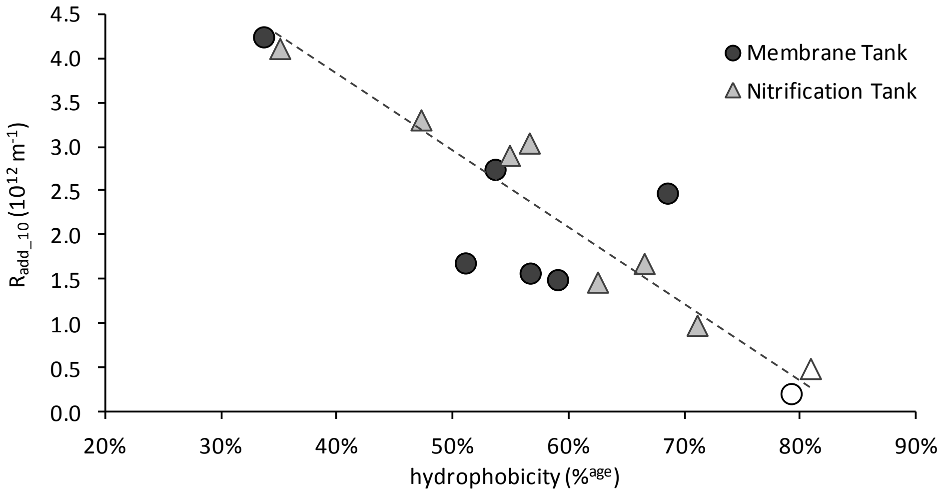

***Figure 8** - Relation between hydrophobicity and R_{add_10}*
(filled datapoints represent sludge samples from January-April and empty datapoint represent samples from June and October).

2.4. Discussion

The sludge samples taken from the full-scale MBR exhibited large variations for all parameters. A distinction could be made between samples taken during the period January-April and samples taken in June and October. Although an effect of iron addition initiated by the end of May cannot be excluded, probably this difference is mainly caused by uncoupling the cheese factory wastewater at the beginning of May. As a direct response the permeability of the membranes in the full-scale MBR improved considerably (STOWA, 2006). Also the filterability of the sludge improved. However, the filterability of the wastewater did not show a similar improvement, indicating that the polymer in the cheese factory wastewater had an indirect effect on sludge filterability, i.e. only after it had been in contact with the sludge.

The strongest correlations between sludge quality and filterability were found for (1) constituents in the supernatant bigger than 0.45 µm, i.e. the colloidal fraction of the supernatant, (2) in particular the polysaccharide concentration in this fraction, (3) the hydrophobicity of the sludge flocs and (4) the organic content of the sludge. Remarkably, whereas a strong correlation was shown between the colloidal fraction and sludge filterability, such a correlation did not exist between sludge concentration and filterability. Literature gives conflicting information on the effect of sludge concentration (e.g. Itonaga *et al.*, 2004, Meng *et al.*, 2005, Cho *et al.*, 2004, Le-Clech *et al.*, 2003 and Chang & Kim, 2005). Sometimes a strong correlation is reported while in other case no correlation could be detected at all. The present study showed that the effect of sludge concentration is less important than the effect of the supernatant. This is also confirmed by other studies (e.g. Bouhabila *et al.*, 2001, Rosenberger *et al.*, 2002, Itonaga *et al.*, 2004, Lesjean *et al.*, 2005, Laabs *et al.*, 2004 and Fan *et al.*, 2006). A comparison of filterability of supernatant to that of the 0.45 µm filtered supernatant reveals that the colloidal fraction has the largest contribution to fouling resistance. In addition, a comparison with wastewater filterability indicates that this colloidal fraction leading to fouling does not originate from the wastewater but is produced during the biological treatment process. A more detailed characterization of the supernatant showed that in particular high concentrations of polysaccharides coincide with a poor filterability. A similar correlation was found by others (Lesjean *et al.*, 2005 and Rosenberger *et al.*, 2006). In the full-scale MBR of Varsseveld it was established that these polysaccharide concentrations were much lower in the period after uncoupling the cheese factory wastewater.

The above leads to the conclusion that measures to counteract membrane fouling should focus on a reduction of the colloidal polysaccharide concentration. The interplay between flocculation and deflocculation is very important in this because the strength of the sludge flocs dictates the equilibrium between these two processes and herewith the concentration of colloidal matter. Literature about this topic is scarce, although it is known that the equilibrium can be manipulated by mixing intensity and oxygen concentration: a lower mixing intensity and higher dissolved oxygen concentration have a positive effect on floc formation and reduce the concentration of colloids. Also other factors such as anaerobic and anoxic contact times and the presence of Fe^{3+} may be important (e.g. Wilén & Balmer, 1999, Wilén *et al.*, 2003, Wilén *et al.*, 2004 and Jin *et al.*, 2004). One of the possibilities to reduce the concentration of colloidal matter is to apply specific additives such as synthetic organic polymers (e.g. Yoon *et al.*, 2005).

A strong positive correlation was also found between hydrophobicity and filterability. A higher hydrophobicity generally is considered essential for stronger flocs which are less sensitive to defragmentation and deflocculation (e.g. Mikkelsen & Keiding, 2001, 2002a and 2002b). Probably also the concentration of polysaccharide EPS is important because by their hydrophilic character they may induce a lower (in-floc) hydrophobicity. Samples taken in June and October exhibited a low concentration of bound polysaccharides which matched with a high hydrophobicity and good filterability. However, at the same time the average particle size of the sludge in this period was relatively small, which is in conflict with most of the literature stating that larger particles give a better filterability. Perhaps a higher density of the flocs is more important than the actual floc size.

A negative correlation was observed between the organic fraction of the sludge and sludge filterability. The lower organic content most likely was caused by the addition of iron chloride to improve phosphorus removal. It is known that Fe^{3+} induces stronger polymeric bridges than Ca^{2+} (Nielsen & Keiding, 1998), which is the multivalent cation most abundantly present in municipal wastewater. This aspect may be important when either chemical or biological phosphorus removal is to be selected in a MBR.

Finally, due to the discharge of the cheese factory wastewater, the situation in Varsseveld was rather unique. Under “normal” conditions perhaps lower colloid concentrations can be expected and therefore questions remains to be answered whether the correlations that were found then still are valid.

2.5. Conclusions

- The constituents in sludge supernatants, and more specifically those larger than 0.45 µm (the colloidal fraction), have the strongest contribution to membrane fouling and do not originate from the wastewater but are produced during the biological treatment process.

- A high degree of hydrophobicity matched with a good filterability, indicating that strong sludge flocs are very important for a good filterability;

- Cheese factory wastewater had a strong negative effect on sludge filterability and caused severe membrane fouling;
- The filterability of the sludge improved considerably after iron chloride addition initiated.

This research has shown that the quality of the sludge is of crucial importance for its filterability, and, more specifically, the concentration of colloidal compounds in the mixed-liquor. It is therefore recommended that future research on membrane fouling in MBR systems focus on methods used to control the concentration colloidal components. In order to keep the colloids to a low level, flocculation of the sludge should be explored as well as methods in order to improve it (e.g. higher dissolved oxygen concentration, multivalent cations, etc…).

2.6. Acknowledgements

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Chapter 3. REDUCTION OF MEMBRANE FOULING BY IMPROVING FLOCCULATION OF ACTIVATED SLUDGE

Maxime Remy[1,2], Hardy Temmink[1,2] and Wim Rulkens[2]

[1.] Wetsus, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

[2.] Wageningen University, Sub-department of Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

Abstract - In this chapter, the relation between flocculation and fouling, obtained from following the Varsseveld MBR in chapter 2, is verified by applying shear on MBR sludge while monitoring filterability and foulants release. Floc disruption was clearly linked to fouling and reflocculation was an efficient way to counter it. Potential ways to counter fouling by influencing the flocculation of the sludge are considered through a short literature study. Addition of powdered activated carbon (PAC) to improve the floc structure and reduce fouling is selected. PAC addition to a MBR has already been studied in the past. The literature on this subject is summarized with the effects and drawbacks in order to find an optimal dosing approach keeping the costs moderate.

Keywords - membrane bioreactor; MBR; membrane fouling; activated sludge; flocculation; powdered activated carbon; PAC

3.1. Introduction

Based on the results of an extensive monitoring session during the start-up of a full-scale membrane bioreactor (MBR) treating municipal wastewater, it was hypothesized that membrane fouling is closely related to the strength and stability of the activated sludge flocs (chapter 2). Under conditions of good flocculating sludge, membrane fouling also is limited because the concentrations of potential membrane foulants such as floc fragments and free extracellular polymers (EPS) are low (Figure 1).

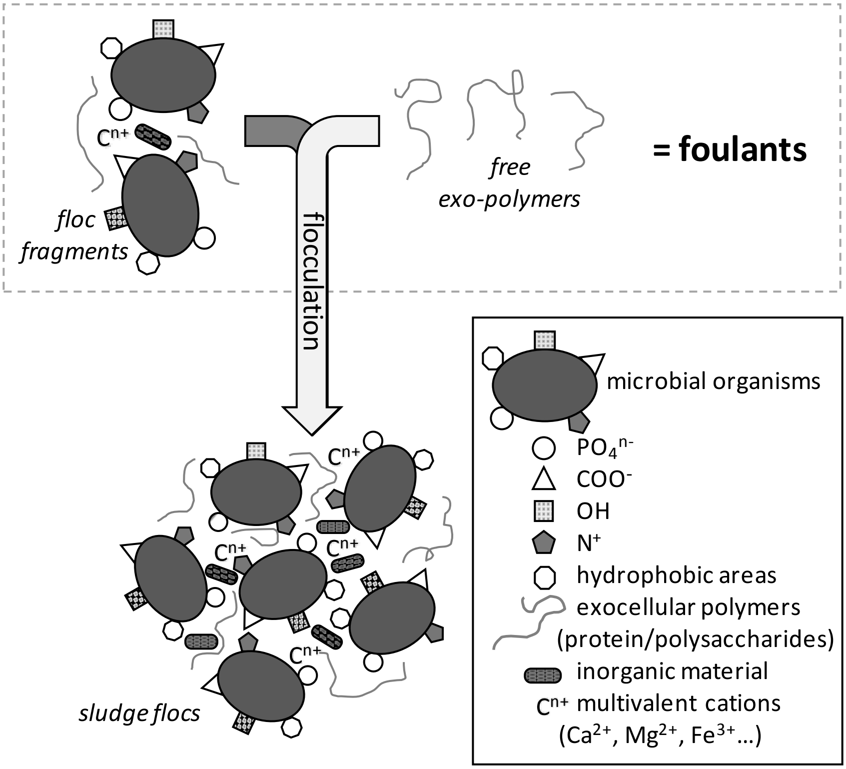

Figure 1 - *Schematic representation of an activated sludge floc and potential membrane foulants.*

However, the full-scale MBR in chapter 2 was subjected to a lot of variation in wastewater composition and temperature, and for an extended period even received industrial wastewater containing high concentrations of suspected membrane foulants. Therefore, to verify the assumption that flocculation is the key mechanism determining the level of membrane fouling, in this chapter a simple laboratory experiment was performed under more controlled and stable conditions. In this experiment, sludge from a pilot-scale MBR was subjected to a high degree of shear to induce floc disruption and the effect of this on sludge filterability was determined. Also the effect of re-flocculation on sludge filterability was investigated, i.e. after the extra shear had been removed.

Because this experiment clearly demonstrated the importance of flocculation, a literature study was performed to identify possible measures to improve sludge flocculation and herewith reduce membrane fouling in MBR systems. From this literature study the addition of low concentrations of powdered activated carbon (PAC) was selected as the most promising and economically viable strategy. Although the addition of PAC to MBR systems is not new, we have chosen to add only very low concentrations of PAC, in combination with a relatively long sludge retention time (SRT) to minimize wasting of this PAC with the excess sludge. The effect of this strategy on sludge filterability and membrane fouling is the topic of the next chapters.

3.2. Experiment to demonstrate the effect of flocculation on sludge filterability

3.2.1. Material and methods

A pilot-scale MBR with a total working volume of 85 L was fed with municipal wastewater. The sludge retention time (SRT) was maintained at 25 days. More details on the operation of this MBR can be found in Remy *et al.* (2009). Sludge from the aerobic tank of the MBR was continuously recirculated over five identical filtration vessels placed in series, each with a working volume of 5 L (Figure 2) and a retention time of one hour per vessel. Each vessel contained similar PVDF submerged membranes, with a nominal pore size of 0.03 µm and a surface area of 0.014 m^2.

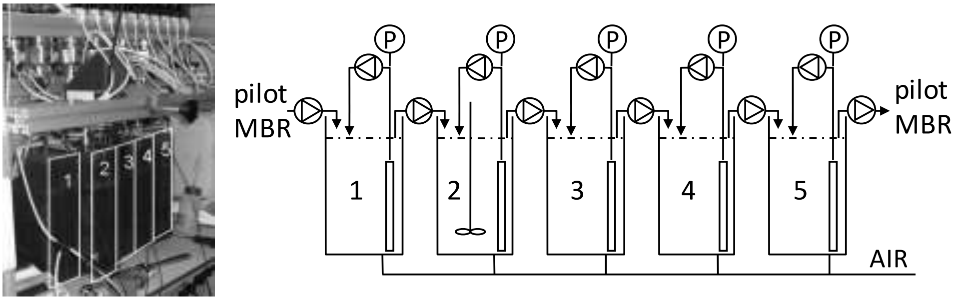

Figure 2 - *Vessels used for the shear test and to determine sludge filterability.*

The membrane vessels were equipped with a coarse bubble aerator to scour the membrane surface at a flow rate of 6.6 L min^{-1}. This corresponds to a specific aeration demand (SAD) of 28 m^{3} m^{-2} h^{-1}. This is very high compared to full-scale MBR systems to compensate for the broad channel width and the small surface area of the membranes. The trans membrane pressure (TMP) was monitored on-line (Endress+Hauser, Cerebar M PMC 41) as an indication of membrane fouling. Permeate was extracted with a peristaltic pump at a constant flux of 50 L m^{-2} h^{-1}, and recirculated to the membrane vessels for a period of 24 hours. After the last vessel, the sludge mixture was fed to the aerobic reactors of the pilot-scale MBR. An overhead mixer with a single blade propeller was installed in vessel number two and operated at 1200 rpm, which corresponds to approximately 1200 s^{-1} (Mikkelsen & Keiding, 2002a), to induce sufficient shear to disrupt the flocs in vessel 2, and give a potential release of membrane foulants.

Sludge was sampled in each tank after 16 hours of recirculation. Supernatant was obtained from these sludge samples with a centrifuge (Sigma, 2-16), operated at 3500 rpm for 15 minutes to remove the solids. After centrifugation, paper filtrate was obtained with a Whatman Black Ribbon filter (589/1, 12-25 µm). The soluble fraction was obtained using Cronus PTFE syringe filter with a nominal pore size of 0.45 µm. The difference between paper filtrate and the filtrate of the 0.45 µm filter will be referred to as the colloidal fraction of the supernatant. Chemical oxygen demand (COD) of the different fractions was determined according to standard methods (APHA-AWWA-WEF, 1998).

3.2.2. Results and discussion

Figure 3 shows the TMP development in the five vessels during the experiment. Each of the membranes in the vessels had a starting TMP of 29 mbar. The sludge in vessel 2, where the extra shear was introduced, clearly resulted in the highest TMP, i.e. an increase of 525 mbar within 24 hours. The TMP increase in the other vessels, where the sludge was allowed to reflocculate, was significantly lower and less severe from vessel 3 to vessel 5. In vessel 5 the TMP increase after 24 hours only was 1 mbar. The HRT in each vessel being one hour, the extra retention in each vessel leads to a higher biodegradation and explains the lower TMP in vessels 4 and 5 compared to vessel 1. Furthermore a higher flocculation is expected in those vessels due to a higher DO concentration (not measured) as the relative aeration is higher in the filtration vessels than in the pilot where it was kept at 1.5 mg L^{-1}. Wilmer and Balmer (1999) related an improved flocculation with higher dissolved oxygen concentration.

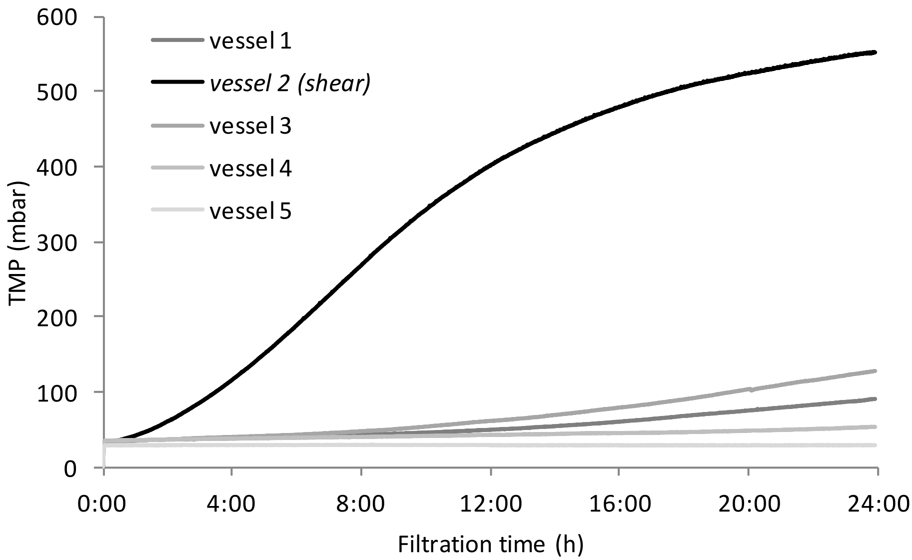

Figure 3 - *TMP development in the five membrane vessels during the shear experiment.*

A clear relation between the TMP increase and the colloidal COD in the sludge after 24 hours was observed (Figure 4), with a significant increase of 7.7 mg L^{-1} in vessel 2, reaching 11 mg L^{-1}, and progressively lower colloidal COD concentrations from vessel 3 to 5, respectively of 6.6, 4.6 and 3.2 mg L^{-1}. The soluble COD concentrations in the different vessels were similar.

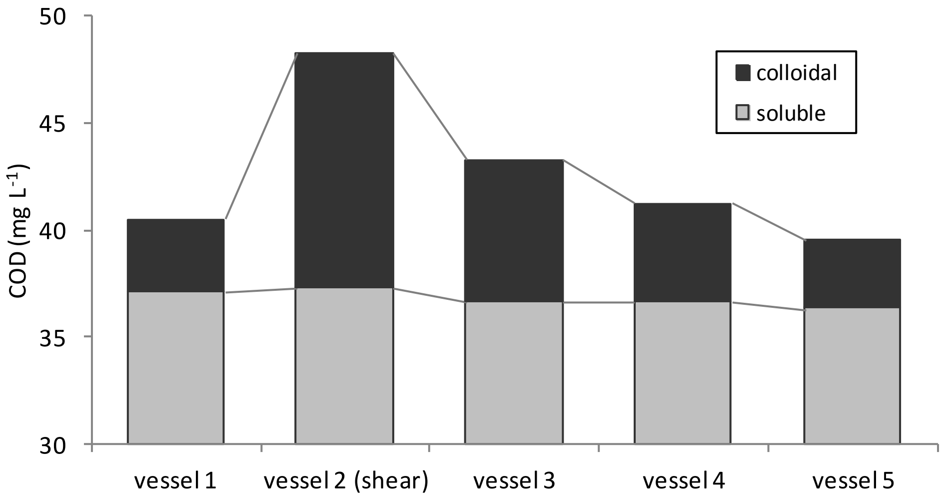

***Figure 4 -** Colloidal and soluble COD in the vessels after 16 hours of enhanced shear in vessel 2.*

These results clearly indicate the relation between flocculation and membrane fouling. Similar to what was observed during the start-up of the full-scale MBR in Varsseveld (chapter 2) the colloidal fraction of the sludge contributes significantly to membrane fouling and should be maintained as low in concentration as possible. Although these results do not provide insight into the exact nature and size of the membrane foulants, which may be free extracellular polymers such as polysaccharides or proteins, clusters of these or even bigger floc fragments (Meng & Yang, 2007), it is obvious that flocculation of the colloidal fraction and herewith flocculation plays a key role in membrane fouling.

3.3. Possibilities to improve flocculation of activated sludge

From a literature survey several possibilities were identified to improve flocculation of activated sludge. These include minimizing the shear on the sludge flocs (Mikkelsen & Keiding, 2002a, Mikkelsen & Nielsen, 2001 and Chaignon *et al.*, 2002), a long SRT (Liao *et al.*, 2001, Lapsidou & Rittman, 2002, Liss *et al.*, 2002 and Nielsen *et al.*, 1997), maintaining high concentrations of dissolved oxygen (DO) (Palmgren *et al.*, 1998, Wilén & Balmer, 1999 and 1998, Wilén *et al.*, 2000 and Wilén *et al.*, 2004) and the addition of multivalent cations such as Ca^{2+} or Fe^{3+} (Urbain *et al.*, 1993, Wilén *et al.*, 2003, Sobeck & Higgins, 2002 and Biggs & Lant, 2001) or organic polymers (Yoon *et al.*, 2005).

A lower degree of shear is in conflict with MBR operation as a certain minimum amount of shear is required in close proximity of the membrane surfaces to be able to prevent severe fouling (Judd, 2011 and Ng *et al.*, 2005). This was also observed by Stricot *et al.* (2010) in laboratory scale MBR systems equipped with side stream membrane modules. Already after a short period of time extremely small biological flocs and even single micro-organisms dominate the particle size distribution, with a dramatic effect on the filterability of the sludge. Nevertheless, options to reduce shear by more efficient mixing of the sludge suspension and a more efficient aeration would provide interesting options to allow for stronger sludge flocs and a lower colloidal fraction.

Although the underlying mechanisms remain unresolved, high DO levels are beneficial for good flocculating sludge. Low DO levels were reported to result in a decrease of the hydrophobicity of different micro-organisms in the sludge flocs (Palmgren *et al.*, 1998). Sustained low DO levels lead to the development of more porous and less compact flocs (Wilén & Balmer, 1999). Also reduction of Fe^{3+} to Fe^{2+} under anaerobic conditions is mentioned as a possible cause of a lower degree of flocculation (Wilén & Balmer, 1998). Fe^{2+} forms weaker bridging bonds than Fe^{3+} between the (extracellular) negatively charged polymers that keep the micro-organisms together. Also a lower production by the micro-organisms of extracellular polymers under anaerobic conditions has been mentioned to explain a lower degree of flocculation at low DO levels. Although high DO levels would yield a better flocculating sludge, it also causes more shear on the sludge flocs because more air needs to be introduced in the sludge mixture. Besides, this would significantly increase the aeration costs and energy consumption of MBR systems.

Although conflicting results have been reported, operation at longer SRTs seems to be another option to obtain strong sludge flocs with a lower membrane fouling propensity (Judd, 2011). At the same time, at long SRTs more mineralization of wastewater organic matter will take place, requiring more aeration (and consequently shear) while the amount of energy that can be gained as biogas when the waste sludge would be digested becomes lower. Longer SRTs (at similar HRTs) also will result in higher sludge concentrations, which makes an energy efficient aeration (and mixing) of the sludge mixture more difficult.

Although a wide range of additives to enlarge and strengthen sludge flocs and to lower free EPS and colloid concentrations is available, their effect has been studied only to a limited extent (Iversen *et al.*, 2009). Addition of synthetic polymers (Yoon *et al.*, 2005 and Koseoglu *et al.*, 2008) and inorganic flocculants such as alum and ferric chloride to reduce membrane fouling generally resulted in an improved filterability (e.g. Lee *et al.*, 2001, Wu *et al.*, 2006 and Koseoglu *et al.*, 2008). This strategy however may be too expensive for municipal wastewater treatment.

3.4. PAC addition to improve sludge filterability

Also the effect of zeolite and PAC addition on membrane fouling has been studied by several researchers. Potential advantages of PAC addition to MBRs were already demonstrated by Kim *et al.* (1998). A better sludge filterability was attributed to a lower compressibility and higher porosity of the cake layer on the membrane surface. However, a short SRT of 6-8 d and a relatively high PAC concentration of 4.1 g L^{-1} were applied. Also Kim and Lee (2003) investigated the effect of PAC addition on membrane fouling in MBRs. The positive effect that was observed was attributed to the adsorption of fine colloids and EPS on the PAC. In external membrane modules a 35% reduction of membrane fouling was obtained and in submerged modules the operational period before membrane cleaning became necessary could be extended threefold. However, these tests were performed with synthetic wastewater, a biological reactor operated at a SRT of 30 days and no less than 6 - 8.3 g L^{-1} of PAC. Ng *et al.* (2005) found that PAC addition yields lower total organic carbon (TOC) concentrations in the membrane permeate and a lower degree of fouling. The latter was proportional to the amount of PAC that was dosed. Short-term tests to determine irreversible fouling indicated an optimum PAC concentration of 5 g L^{-1}. Ying and Ping (2006) found an optimum PAC concentration of 0.75 g L^{-1} with decreasing effects at higher concentrations. The positive effect of PAC was attributed to a lower EPS deposition on the membrane surface, caused by more effective scouring of this surface and adsorption of (free) EPS on the PAC. Fang *et al.* (2006) found that dosing PAC enhances the adsorption of EPS, resulting in a 22% reduction of fouling. However, during long-term trials at extremely long SRTs, the efficiency to prevent membrane fouling decreased significantly in time. The PAC concentration that Fang *et al.* (2006) applied was 2 g L^{-1}.

Although the information above indicates that PAC addition may help to reduce membrane fouling, the associated costs would be very high at the concentrations that were applied. Most concentrations were 5 g of PAC L^{-1} of sludge or above. For example, given a SRT of 10 days, a HRT of 0.5 days and a PAC price of approximately 2 € kg^{-1} (Boere & Van den Dikkenberg, 2006), this would imply costs for the PAC alone of 0.5 € m^{-3} of (municipal) wastewater which seems unacceptably high. In addition, the amount of waste sludge that would be produced at such high PAC concentrations would increase at least by 30%, which leads to even higher overall treatment costs.

3.5. Strategy employed in this study

This study aimed to use PAC at much lower concentrations in the sludge than mentioned above (i.e. 0.5 g L^{-1} compared to 5 g L^{-1}). In combination with a much longer SRT (50 d compared to typically 10 –20 d), this would reduce the costs of PAC addition to only 0.01 € m^{-3} of (municipal) wastewater. The starting point is that such a low concentrations of PAC will serve as a carrier material for activated sludge flocs (Specchia & Gianetto, 1984 and Park *et al.*, 2003), which helps to increase their strength (Figure 5).

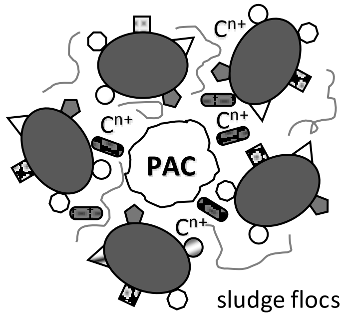

Figure 5 - *Improved floc structure in the presence of PAC.*

For this study meso/macro-porous PAC (average particle size 15 µm, average pore size typically > 2 nm, specific surface area typically < 1200 $m^2\ g^{-1}$) was selected (Boere & Van den Dikkenberg, 2006 and Schouten *et al.*, 2007). In case adsorption of potential foulants such as free EPS in the pore size range of the PAC would be an important mechanism for fouling reduction, this would allow microorganisms access to the adsorbed foulants and offer the possibility for their biodegradation. To maximize the chances for PAC to be included into the flocs and serve as a carrier material, the PAC dosage takes place in the anoxic zone of the MBR. Deflocculation takes place in the zone with lower DO while reflocculation takes place in the zone with highest DO (Wilén & Balmer, 1998 and Wilén *et al.*, 2000) theoretically facilitating the incorporation of the PAC particles into the sludge flocs. An improved inner structure of the flocs, expected with PAC present as a carrier, should result in improved floc strength (Urbain *et al.*, 1993 and Wilén *et al.*, 2003).

The effect of low concentration of PAC in combination with a long SRT on sludge filterability was investigated in this study, both in short-term experiments and in long pilot-scale trials. Also the possible mechanisms explaining the reduction of membrane fouling by PAC addition were investigated. Because the PAC changes the floc structure and possibly lowers the amount of free EPS, it can be expected that it also may change the aeration efficiency of the sludge-mixture and the dewaterability of the excess sludge. As both these parameters are important for an efficient wastewater treatment, they were compared to sludge that was not amended with PAC. A possible additional beneficial effect of PAC is removal of organic micropollutants from municipal wastewater, a topic which at the moment receives a lot of attention. It was established whether the low concentrations of meso/macroporous PAC, while incorporated in the sludge flocs, still have the ability to adsorb such organic micropollutants. Finally, PAC addition may be particularly useful during periods where floc stability is less, for example due to higher wastewater salinity (Sobeck & Higgins, 2002), or lower temperatures (Lishman *et al.*, 2000). This possibility was explored in a number of experiments.

3.6. Acknowledgements

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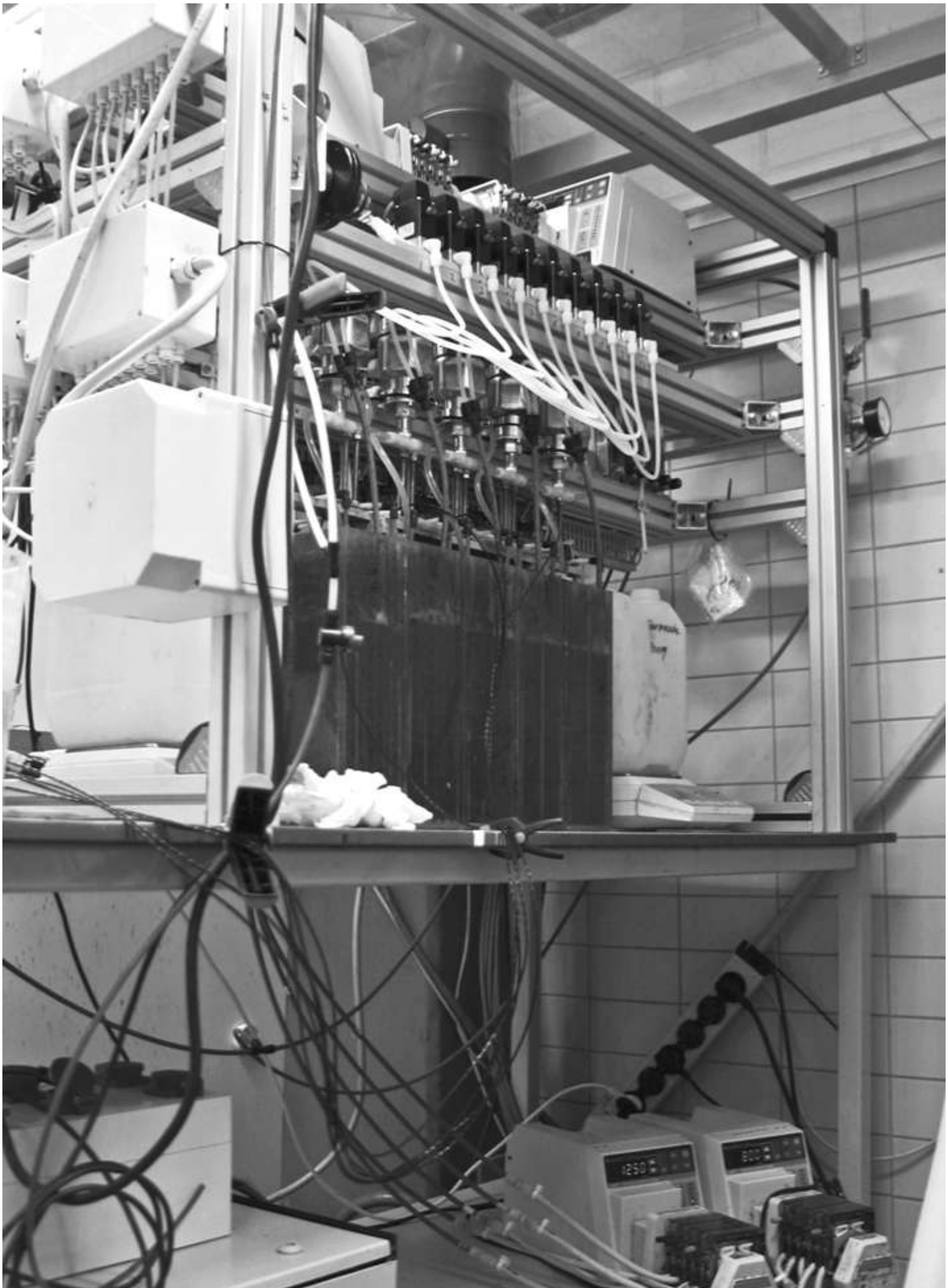

Chapter 4. LOW DOSE POWDERED ACTIVATED CARBON ADDITION AT HIGH SLUDGE RETENTION TIMES TO REDUCE FOULING IN MEMBRANE BIOREACTORS

Maxime Remy[1,2], Perry Van der Marel[1,3], Arie Zwijnenburg[1], Wim Rulkens[2] and Hardy Temmink[1,2]

[1.] Wetsus, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

[2.] Wageningen University, Sub-department of Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

[3.] University of Twente, Membrane Technology Group, P.O. Box 217, 7500 AE, Enschede, The Netherlands

Abstract - The addition of a low concentration of PAC (0.5 g L^{-1} of sludge, i.e. a dose of 4 mg L^{-1} of wastewater), in combination with a relatively long SRT (50 days), to improve membrane filtration performance was investigated in two pilot-scale MBRs treating real municipal wastewater. Continuous filterability tests at high flux showed the possibility to run for 18h at 72L m^{-2} h^{-1} and 180h at 50 L m^{-2} h^{-1}, while significant fouling occurred without PAC. In addition, measurements of the critical flux showed an increase of 10% for this strategy. Low dosage and high retention time makes it feasible and cost effective. Further advantages with regard to permeate quality and possible micropollutants removal are currently under investigation.

Keywords - activated sludge; membrane bioreactor; powdered activated carbon; membrane fouling

Remy, M., Van der Marel, P., Zwijnenburg, A., Rulkens, W. and Temmink, H. (2009), Low dose powdered activated carbon addition at high sludge retention times to reduce fouling in membrane bioreactors, Water Research, Vol. 43, pp. 345-350.

4.1. Introduction

Membrane bioreactors (MBRs) have became common practice for industrial wastewater treatment, because (1) they require a small footprint compared to conventional biological treatment and (2) their effluent is free of solids, often enabling re-use of the effluent as process water. A break-through of MBR technology for municipal wastewater treatment however is seriously hampered by the occurrence of membrane fouling. This results in a large additional energy demand associated with membrane cleaning and/or high investments related to a larger membrane surface area when the membranes are operated at low fluxes to prevent fouling.

For this reason a lot of research has been dedicated to membrane fouling in municipal MBRs, including elucidation of the fouling mechanisms and methods to reduce fouling. An excellent review on these topics is provided by Le-Clech *et al.* (2006). Research to reduce membrane fouling mainly focuses on membrane materials, membrane operation but only to a minor extent on manipulation of the feed sludge characteristics. Large and strong sludge flocs, low concentrations of extracellular polymeric compounds (EPS) and fine colloids all have been mentioned as important sludge characteristics improving sludge filterability (Le-Clech *et al.*, 2006). The results however often are contradictory (Drews *et al.*, 2008 and Rosenberger *et al.*, 2006) and fundamental relationships between sludge characteristics and filterability are not available.

The effect of additives, with the objective to enlarge and strengthen sludge flocs and lower EPS and colloid concentrations, so far has been studied only to a limited extent. Addition of synthetic organic polymers (Yoon & Collins, 2005 and Koseoglu *et al.*, 2008) and inorganic flocculants such as alum and ferric chloride to reduce membrane fouling generally resulted in an improved filterability (e.g. Lee *et al.*, 2001, Wu *et al.*, 2006 and Koseoglu *et al.*, 2008), but this strategy may be too expensive for municipal wastewater treatment. Also the effect of zeolite and powdered activated carbon (PAC) addition on membrane fouling has been studied (Lee *et al.*, 2001, Kim *et al.*, 2003, Li *et al.*, 2005, Fang *et al.*, 2006, Ying & Ping, 2006 and Ng *et al.*, 2006). In particular PAC shows a good potential to reduce membrane fouling. Several mechanisms were mentioned to explain this positive effect, including (1) enhanced scouring of the membrane surface to avoid particle deposition (Park *et al.*, 1999), (2) formation of a more rigid and less compressible cake or gel layer (Pirbazari *et al.*, 1996), (3) adsorption of membrane foulants such as soluble EPS by the PAC (Fang *et al.*, 2006) and (4) an improved flocculation (Li *et al.*, 2005).

Although the results with PAC look promising, generally high PAC dosages, which would be too costly for municipal wastewater treatment, were applied. Besides, often synthetic wastewater was used in the experiments, which does not represent practical conditions. In this study we therefore investigated the effect of a low PAC dosage, in combination with relatively long sludge retention on the filterability of the sludge in a pilot-scale municipal MBR. According to our estimations a PAC concentration of 0.5 g L^{-1} sludge (*i.e.* dosage of 4 mg of PAC L^{-1} of wastewater), combined with the high sludge retention time, would result in acceptable additional costs of € 0.008 m^{-3} treated wastewater, given PAC cost of € 2 kg^{-1}.

4.2. Material and Methods

4.2.1. Pilot-scale MBRs

Two identical pilot-scale MBRs (Figure 1), each with a total working volume of 85 L, were operated in parallel and fed with municipal wastewater. This wastewater was screened (5 mm) before entering the biological reactors. The COD of the wastewater was 300 mg L^{-1} on average, but fluctuated between 150 and 600 mg L^{-1}. Table 1 shows the COD of the wastewater in the different fractions, for the different periods. The overall hydraulic retention time (HRT) of the MBRs was 10 h, with 4.1 h for the anoxic tank, 4.1 h for the aerobic and 1.8 h for the membrane tank. The recirculation ratio from the aerobic to the anoxic tank was 4 and 12 from the membrane tank to the aerobic tank. The oxygen concentration in the aerobic tank was measured on-line and controlled at 1.5 mg L^{-1} with a fine-bubble diffuser.

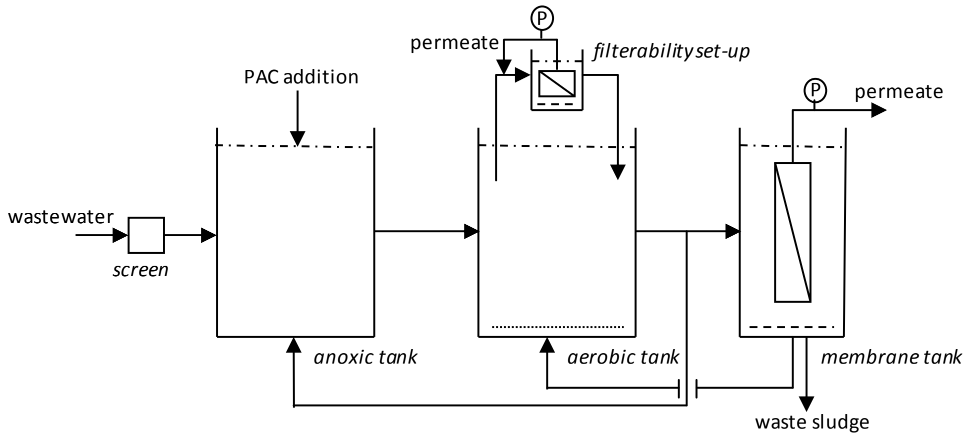

Figure 1 - *Pilot-scale MBR and set-up to measure filterability and critical flux.*

COD (mg L^{-1})	Monitoring period I		Monitoring period II	
	average	std	average	std
Total	242	80	323	251
Paper Filtered	75	19.7	100	4.5
Soluble	61.7	1.8	66.4	3.3

Table 1 - *Wastewater characteristics during the monitored periods.*

The membrane tank was equipped with five homemade submerged PVDF flat sheet membranes with a nominal pore size of 0.2 µm and a surface area of 0.1 m^2 each. The channel width between the membranes was 6 mm. Coarse bubble aerators placed below the membranes provided 10 L min^{-1} of air to scour the membrane surface and reduce fouling. This corresponds to a specific aeration demand (SAD) of 1.2 $m^3\ m^{-2}\ h^{-1}$, which is within the range for full scale submerged flat sheet MBR installations (Judd, 2006). With a peristaltic pump, permeate was extracted continuously at a flux of 17.4 L $m^{-2}\ h^{-1}$. This flux is in the range of fluxes of 15 - 25 L $m^{-2}\ h^{-1}$ applied in full-scale municipal MBRs equipped with submerged membranes, and is generally considered to be well below the critical flux causing cake layer formation. The trans-membrane pressure (TMP) was measured on-line with pressure transducers (Endress+Hauser, Cerebar T PMC 131).

4.2.2. PAC addition and SRT

Before the start of the monitoring period I both the pilot-plants A and B were operated for more than 6 months, respectively at SRTs of 25 and 50 days (Table 2). To achieve a PAC concentration of 0.5 g L^{-1} of sludge, in pilot-plant B operated at a SRT of 50 days SRT daily 0.8 g of mesoporous Norit SAE Super PAC (specific surface area 1150 m^2 g^{-1}, particle size D_{50} of 15 µm) was added to the anoxic tank. In this manner during monitoring period I sludge filterability and critical flux during conventional operation at SRT 25 days could be compared to the combination of low PAC addition and a relatively long SRT of 50 days. After a monitoring period of 1.5 months, the SRT of the pilot-plant operated at 25 days without PAC addition was changed to 50 days to investigate the effect of PAC independently of the SRT in monitoring period II. Monitoring period II started 4 months after the end of period I to adapt the sludge of reactor A to 50 days SRT.

monitoring period	MBR A		MBR B	
	SRT (d)	PAC (g L^{-1} sludge)	SRT (d)	PAC (g L^{-1} sludge)
I	25	0	50	0.5
II	50	0	50	0.5

Table 2 - *Pilot-plant operation.*

4.2.3. Sludge filterability

Sludge from each of the aerobic reactors of the two pilot-plants was continuously recirculated over a separate membrane vessel with a volume of 5 L (Figure 1). These vessels contained two flat-sheet PVDF submerged membranes, similar to the ones used in the pilot-plants, but each with a much lower surface area of 0.014 m^2. Membranes were chemically cleaned between the measurements with NaOCl at a concentration of 3000 ppm to remove organics that may have deposited on the membrane. The small membrane tanks in the filterability unit were equipped with a coarse bubble aerator to scour the membrane surface at a flow rate of 6.6 L min^{-1}. This corresponds to a SAD of about 28 m^3 m^{-2} h^{-1}. This SAD is very high compared to practice, but this is to compensate for the broad channel width and the small surface area of the membranes used for these tests. The TMP was monitored on-line (Endress+Hauser, Cerebar M PMC 41). To determine sludge filterability, permeate was extracted with a peristaltic pump at a constant high flux of 50 or 72 L m^{-2} h^{-1}, and was recirculated to the membrane vessel. The sludge mixture was returned to the aerobic reactors of the pilot-plant.

4.2.4. Critical flux

In addition to sludge filterability, the critical flux was determined using a flux-step method proposed by Van der Marel *et al.* (2009), consisting of cycles with 15 minutes permeation at a relatively large flux followed by 15 min relaxation at a low flux of 5 L m^{-2} h^{-1}. The flux was increased every consecutive cycle by 5 L m^{-2} h^{-1}, up to a maximum level of 105 L m^{-2} h^{-1}. The critical flux was arbitrarily defined as the flux above which the rate of TMP increase exceeded 0.1 mbar min^{-1} (Van der Marel *et al.*, 2008). The fouling rate, i.e. the increase of the total filtration resistance in time, was calculated at each flux step according to:

$$F = \frac{dR}{dt} = \frac{1}{\eta J}\frac{dTMP}{dt}$$

with F the fouling rate (m^{-1} s^{-1}), R the resistance (m^{-1}), TMP the trans-membrane pressure (Pa), η the viscosity (Pa s), J the flux (m^3 m^{-2} s^{-1}) and t the time (s). The same setup as the one used for sludge filterability was used for critical flux determinations.

4.2.5. Chemical analyses

COD, suspended solids (SS) and volatile suspended solids (VSS) were all determined according to standard methods. Concentrations of polysaccharides and proteins were determined according to the methods of Dubois *et al.* (1956) and Bradford (1976) respectively using Glucose and Immunoglobulin G as standards.

4.3. Results

4.3.1. General observations

Average total solids concentrations in the two membrane tanks of the pilot-scale MBRs were relatively constant with an average of 11.8 and 13.6 g L^{-1}, respectively in MBR A without PAC addition and MBR B with PAC addition. During the entire monitoring period no significant differences could be observed in permeability of the membranes in the pilot-scale plants. Mechanical and chemical cleanings were not required as the TMP always remained below 20 mbar. Apparently fouling was very low at the relatively low flux of 17.4 L m^{-2} h^{-1}, irrespective of the addition of PAC and the SRT. Nevertheless, when cleaning the membranes at the end of monitoring periods I and II, a visible gel layer was present on the surface of the membranes in MBR A without PAC addition, both at a SRT of 25 days and a SRT of 50 days, whereas a visible gel layer was absent in MBR B with PAC addition.

4.3.2. Permeate quality

Average permeate quality with respect to COD, polysaccharides and proteins generally was better in the MBR operated with PAC compared to the MBR operated without PAC (Table 3). Although the differences were small, in particular during monitoring period II when both MBRs were operated at a SRT of 50 days, they were consistent. Adsorption of COD by PAC seems a likely explanation for the improved permeate quality but other mechanisms cannot be excluded.

parameter		monitoring period I		monitoring period II	
		SRT 25 d no PAC (A)	SRT 50 d PAC (B)	SRT 50 d no PAC (A)	SRT 50 d PAC (B)
COD	mg L^{-1}	36	30	33	30
polysaccharides	mg L^{-1}	6.0	3.7	7.4	6.9
proteins	mg L^{-1}	4.3	3.6	3.7	3.4

Table 3 - *Average permeate quality with respect to COD, polysaccharides and proteins.*

4.3.3. Sludge filterability

Figure 2 compares the TMP increase during continuous filtration at 72 L m^{-2} h^{-1} with MBR A sludge operated at 25 days SRT without PAC addition, and with MBR B sludge operated at 50 days SRT with 0.5 g PAC L^{-1} in monitoring period I. Whereas with MBR B sludge the TMP increase was less than 10 mbars over a period of 18 h, with MBR A sludge the TMP within 1 hour started to increase and reached more than 500 mbars after 18 h of filtration. To exclude errors in the test set-up, the filtration tests were repeated after exchanging the membrane vessels between the pilot-plants. This gave similar results with superior filtration behavior of MBR B sludge.

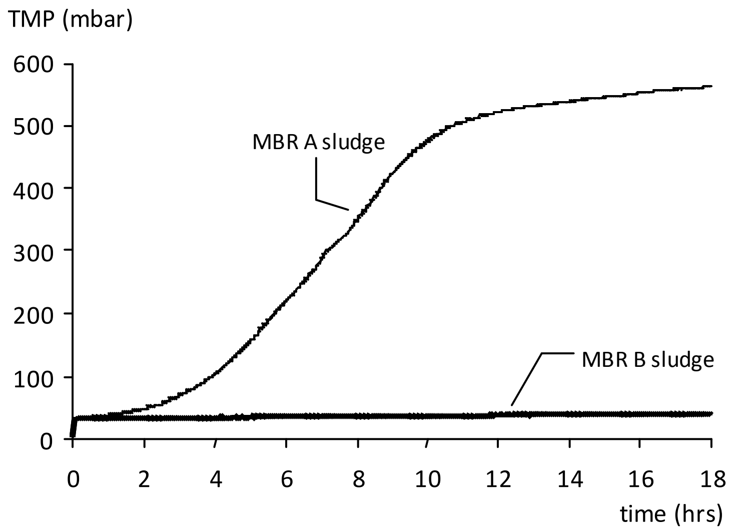

Figure 2 ***-*** *TMP development in the filterability set-up operated at 72 L m^{-2} h^{-1} with MBR A sludge (SRT of 25 days, no PAC) and MBR B sludge (SRT of 50 days, 0.5 g PAC L^{-1} of sludge).*

A similar test was carried in monitoring period II out at a flux of 50 L m^{-2} h^{-1} to compare sludge operated at 50 days without (MBR A sludge) and with PAC (MBR B sludge) addition (Figure 3). Because the filterability seemed to be lower than during monitoring period I, a somewhat lower flux was applied and a relaxation period at zero flux was included of 30 minutes after every 4.5 h of permeation. In addition, a much longer overall filtration period of 160 h was applied. Filtration of MBR B sludge, operated at 50 days SRT with 0.5 g PAC L^{-1}, even after a period of 160 h did not result in a significant increase of the TMP. In contrast, MBR A sludge also operated at 50 days SRT but without PAC, after a delay of approximately 70 h exhibited a sharp increase in TMP to reach more than 600 mbars after 160 h of filtration. Again, a similar result was found after the filterability set-up had been exchanged between the two pilot-plants.

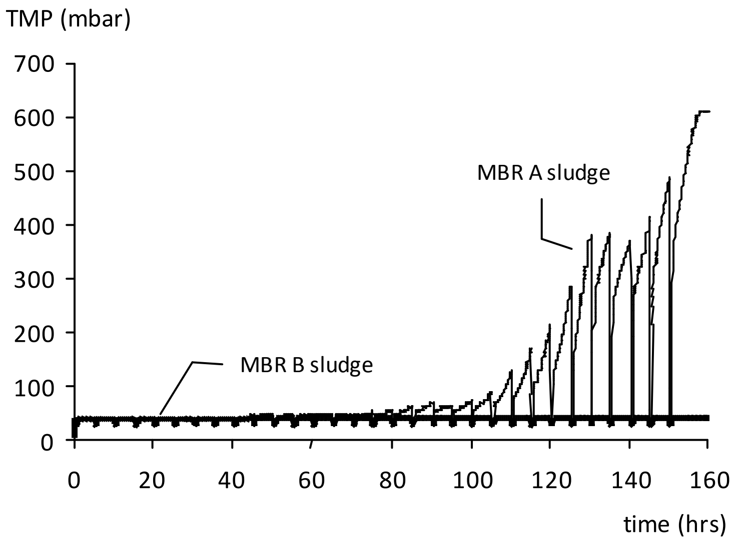

Figure 3 - *TMP development in the filterability set-up operated at 50 L m^{-2} h^{-1} (including relaxation at zero flux for 30 min every 4.5 h) with MBR A sludge (SRT of 50 days, no PAC) and MBR B sludge (SRT of 50 days, 0.5 g PAC L^{-1} of sludge).*

The same filterability tests were also performed with commercial chlorinated polyethylene (PE) membranes, with the same surface area and a nominal pore size of 0.4 µm (data not shown). This time, MBR B sludge exhibited a TMP increase of only 10 mbars after 160 h filtration time, whereas (like for the homemade PVDF membranes) filtration of MBR A sludge with the PE membranes gave an increase of TMP of more than 600 mbars. The membrane surfaces were inspected visually after every filterability experiment and cleaned by rinsing with permeate. Without any exception, always a gel layer was observed. However, the gel layers formed during filtration of sludge with PAC always were much easier to remove than the gels formed during filtration of sludge without PAC.

The phenomenon that PAC improves the filterability of sludge also was reported by Kim and Lee (2003). They used a submerged PE membrane with a pore size of 0.1 µm to show that sludge samples inoculated with PAC could be operated 3 times longer before a TMP was reached of 300 mbars compared to sludge samples without PAC. However, they used sludge that was cultivated with synthetic wastewater rather than with real municipal wastewater. Furthermore, the PAC concentration they applied was higher (2 compared to 0.5 g L^{-1} in our experiments) and the membrane flux they applied was much lower (15 L m^{-2} h^{-1} compared to 50 and 72 L m^{-2} h^{-1} in our experiments).

4.3.4. Critical flux

Figure 4 shows an example of a filtration run in the filterability set-up to determine the critical flux by consecutive cycles consisting of 15 minutes at a high flux and a relaxation period of 15 minutes at a flux of 5 L m^{-2} h^{-1}. This example clearly demonstrates that MBR A sludge operated at 50 days SRT without PAC above a flux of approximately 60-70 L m^{-2} h^{-1} starts to exhibit a much larger TMP increase than MBR B sludge also operated at 50 days SRT but with 0.5 g L^{-1} of PAC. In both cases, relaxation at a flux of 5 L m^{-2} h^{-1} resulted in a steady base line TMP of 25-30 mbars, indicating that the fouling had a reversible character. This base line TMP corresponds with the pressure due to the water column between the surface of the water in the setup and the pressure controllers situated at a higher level.

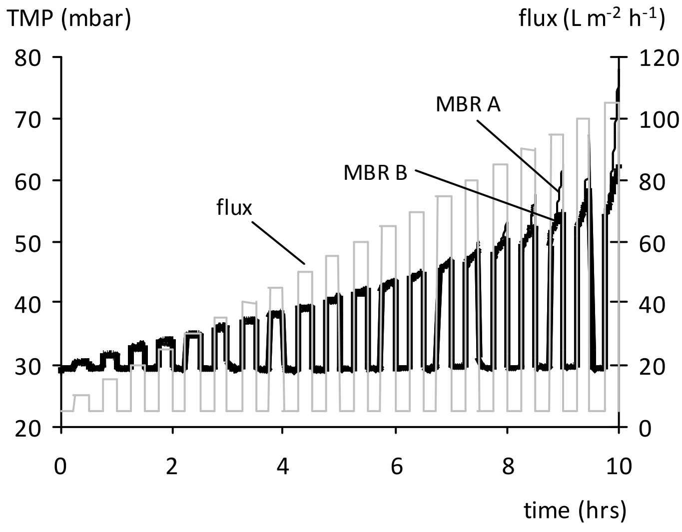

Figure 4 *-TMP development during the flux-step method to determine of the critical flux with MBR A sludge (SRT of 50 days without PAC) and MBR B sludge (SRT of 50 days with 0.5 g PAC L^{-1}).*

At each flux the fouling rate was determined, and according to equation (1) and with the cut-off value of 0.1 mbars min^{-1} a critical flux was established. The results are shown in Figures 5 and 6, respectively comparing MBR A sludge and MBR B sludge during monitoring periods I and II (Table 1). The figures represent averages collected from 4-6 runs with interchanging the membranes and aerators in between, to avoid possible errors introduced by unknown slight differences in system configuration. Figure 5 shows that MBR A sludge operated at 25 day SRT sludge without PAC addition crosses the critical fouling rate at a flux of 92 L m^{-2} h^{-1}. This is 11% lower than the critical flux of 102 L m^{-2} h^{-1} determined for MBR B sludge operated at 50 days SRT with addition of 0.5 g L^{-1} of PAC. These relatively high critical fluxes compared to literature data probably were caused by the low fouling propensity of the homemade PVDF membranes that were used in this study.

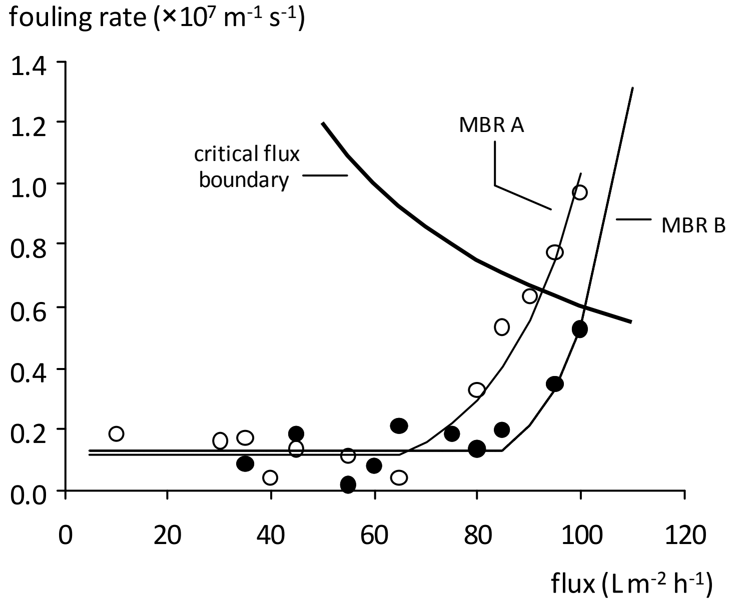

Figure 5 *- Effect of the flux on the fouling rate with MBR A sludge (SRT of 25 days, no PAC) and MBR B sludge (SRT of 50 days, 0.5 g PAC L^{-1}) in monitoring period I.*

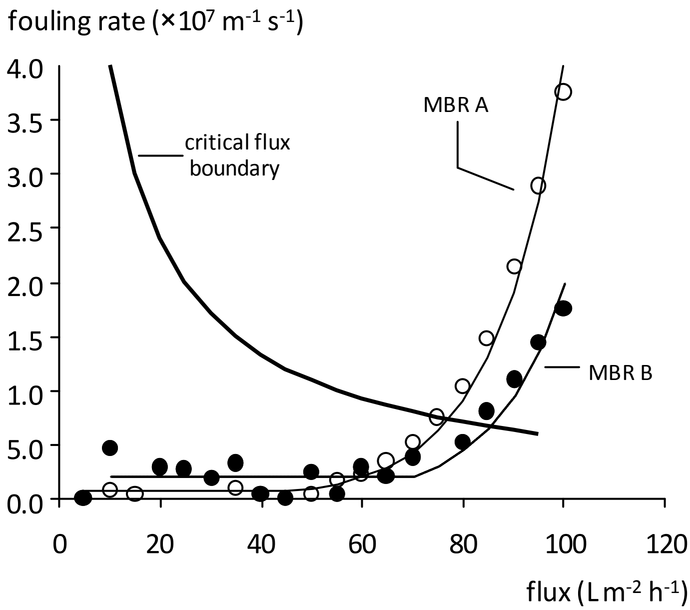

Figure 6 - *Effect of the flux on the fouling rate with MBR A sludge (SRT of 50 days, no PAC) and MBR B sludge (SRT of 50 days, 0.5 g PAC L^{-1}) in monitoring period II.*

Similarly, as shown in Figure 6, the critical flux for MBR A sludge operated at 50 days SRT without PAC is 76 L m^{-2} h^{-1}, i.e. 11% lower than the critical flux of 85 L m^{-2} h^{-1} for MBR B sludge operated during the same period at the same SRT of 50 days but with 0.5 g L^{-1} of PAC. It should be remarked however that both these critical fluxes are significantly lower than in monitoring period I (Figure 5). This may have been caused by the lower ambient temperature of 18.2 °C in period II compared to 23.6 °C during period I.

Also Li *et al.* (2005) reported a positive effect of PAC on the critical flux, although they applied a higher PAC dosage (1.2 g L^{-1}), a shorter SRT (30 days) and synthetic wastewater rather than real municipal wastewater. Even though the differences in critical flux between sludge with and without PAC in our experiments only were 11%, apparently with PAC this already translates to a much longer period of membrane operation at a high flux in the absence of fouling, as was demonstrated in Figures 3 and 4.

4.4. Discussion

The experiments focused on the feasibility of PAC addition to improve the filtration performance in municipal MBRs. It was clearly demonstrated that sludge filterability as well as critical flux improved significantly, already at a low dosage of PAC of 0.5 g L^{-1} of sludge (4 mg of PAC L^{-1} of wastewater). In combination with a relatively long SRT of 50 days, and assuming PAC costs of € 2 kg^{-1}, it was estimated that the additional operational costs would be limited to only € 0.008 per m^3 of wastewater.

The pilot-scale MBRs were operated at a flux of 17.4 L m^{-2} h^{-1}, which is within the range of fluxes of 15-25 L m^{-2} h^{-1} that is applied in full-scale MBRs and well below critical fluxes leading to cake layer formation. The next step will be to investigate how high a flux can be applied for long periods without fouling in the pilot-scale MBR itself. Based on the results it is expected that at a low PAC dosage a flux of typically 40 - 60 L m^{-2} h^{-1} can be maintained without significant fouling.

It should also be investigated whether higher fluxes are possible at even lower PAC dosages than 0.5 g L^{-1}. Ng *et al.* (2006) investigated the effect of PAC concentration on membrane fouling in a dead-end filtration test with sludge cultivated with synthetic wastewater. A PAC concentration of 1 g L^{-1} resulted in considerably lower reversible membrane fouling than higher PAC concentrations of 3 and 5 g L^{-1}, indicating that low PAC dosages may be better than high PAC dosages. However, they also observed that to prevent irreversible fouling a PAC dosage of 5 g L^{-1} was required. In our long-term continuous filtration experiments no irreversible fouling was detected and therefore higher PAC dosages than 0.5 g L^{-1} do not seem to be justified.

An additional advantage of PAC addition may be the removal of organic micropollutants from municipal wastewater. Currently several post-treatment technologies, including activated carbon treatment, are investigated for this purpose. Addition of PAC to the biological reactor may prevent the necessity of such an expensive post-treatment step, although it is not known whether a sufficient degree of adsorption, possibly in combination with biological regeneration of the PAC, can be accomplished. Other aspects which need to be investigated are the effect of low PAC dosages on the oxygen transfer and on sludge digestibility.

The question why PAC already at low dosages has a positive effect on filterability of (municipal) MBR sludge remains unclear. Still this questions needs to be answered. For instance, we selected mesoporous rather than microporous PAC for the experiments because this would make adsorption of membrane foulants, reported by Fang *et al.* (2006), easier accessible for subsequent biodegradation. Apart from adsorption of membrane foulants, also the formation of stronger flocs mentioned by Lee *et al.* (2005) could explain the positive effect of PAC. This however would not justify the application of PAC as in this case other, cheaper materials such as sand or bentonite could also be used to promote flocculation. Other mechanisms mentioned in the literature are enhanced scouring of the membrane surface, albeit the PAC is incorporated in the sludge flocs, and the formation of a less compressible and more rigid gel- and/or cake-layer. Which mechanism or combination of mechanisms dictates the positive effect of PAC on sludge filterability is currently under investigation.

4.5. Conclusion

The effect of PAC was investigated in two pilot-scale MBRs treating municipal wastewater. It was shown that the combination of a low PAC dosage (0.5 g L^{-1} of sludge), with a relatively long SRT of 50 days resulted in:

- an improvement of the critical flux of around 10%,
- a strong increase of the filtration period without significant fouling at high fluxes of 50-72 L m^{-2} h^{-1},
- a decrease of gel deposition on the membrane surface after a long filtration period,
- an easier removability of gels deposited at high fluxes and
- a slight increase of the permeate quality.

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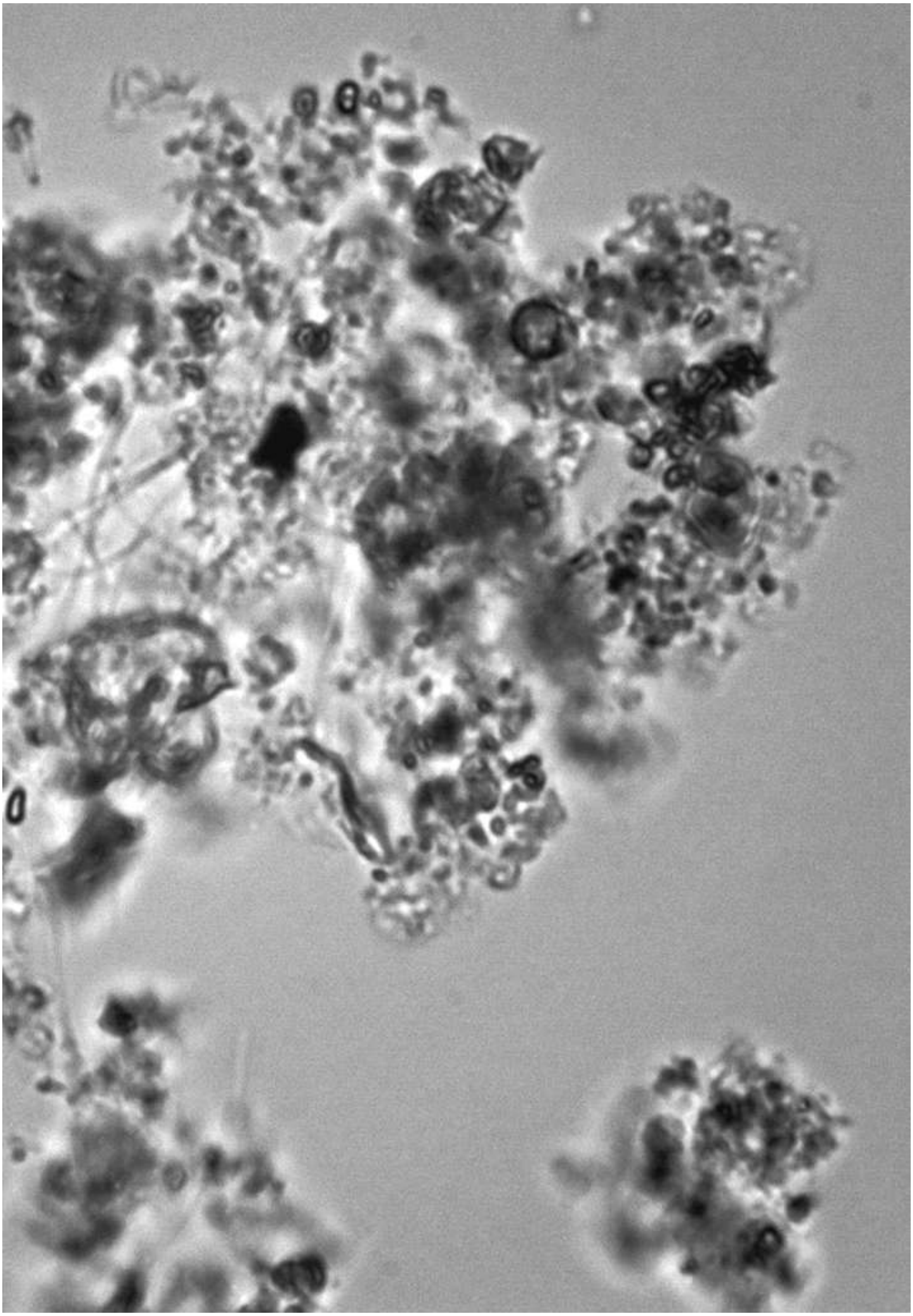


Chapter 5. WHY LOW POWDERED ACTIVATED CARBON ADDITION REDUCES MEMBRANE FOULING IN MBRS

Maxime Remy[1,2], Virginie Potier[1], Hardy Temmink[1,2] and Wim Rulkens[2]

[1.] Wetsus, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

[2.] Wageningen University, Sub-department of Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

Abstract - Previous research had demonstrated that powdered activated carbon (PAC), when applied at very low dosages and long SRTs, reduces membrane fouling in membrane bioreactor (MBRs). In this contribution several mechanisms to explain this beneficial effect of PAC were investigated, including enhanced scouring of the membrane surface by PAC particles, adsorption of membrane foulants by PAC and subsequent biodegradation and a positive effect of PAC on the strength of the sludge flocs. It was concluded that the latter mechanism best explains why low dosages of PAC significantly reduce membrane fouling. Cheaper alternatives for PAC may have a similar effect.

Keywords - membrane fouling; membrane bioreactor; powdered activated carbon; adsorption; flocculation; filterability

Remy, M., Potier, V., Temmink, H. and Rulkens, W. (2010), Why low powdered activated carbon addition reduces membrane fouling in MBRs, Water Research, Vol. 44, pp. 861-867.

5.1. Introduction

Although membrane bioreactors (MBRs) offer several advantages compared to conventional treatment systems (Judd, 2006), their widespread application is seriously hampered by the higher operational and capital costs associated with membrane fouling. Important factors determining membrane fouling in MBRs are membrane properties, module design and the composition and filterability of the mixed-liquor suspended solids (Le-Clech *et al.*, 2006 and Meng *et al.*, 2009). Several additives have been tested to reduce membrane fouling in MBRs, and generally this resulted in an improved filterability, but also in a substantial increase of the operational costs. These additives include organic polymers (e.g. Kim *et al.*, 2001, Yoon & Collins, 2005, Koseoglu *et al.*, 2008 and Iversen *et al.*, 2009) and inorganic flocculants such as alum and ferric chloride (e.g. Lee *et al.*, 2001, Wu *et al.*, 2006 and Koseoglu *et al.*, 2008). The effect of particles such as zeolite or powdered activated carbons (PAC) also have been successfully applied (e.g. Park *et al.*, 1999, Lee *et al.*, 2001, Kim & Lee, 2003, Li *et al.*, 2005 and Fang *et al.*, 2006), albeit at relatively high concentrations. Remy *et al.* (2009) showed that a low PAC dosage of only 0.5 g L^{-1} of sludge, combined with a long sludge retention time (SRT), namely 50 days, effectively reduced fouling in a pilot-scale MBR, while the increase of operational costs associated with PAC addition could be kept as low as € 0.008 m^{-3} treated wastewater.

Several mechanisms to explain the positive effect of PAC on filterability were mentioned in the literature, all related to relatively high PAC concentrations and/or a specific application, for example in anaerobic or industrial MBRs. Pirbazari *et al.* (1996) observed that a PAC concentration of 10 g L^{-1} in a cross-flow ultrafiltration-MBR treating high strength landfill leachate resulted in less fouling. They explained this effect by the deposition of a dynamic and permeable PAC layer on the surface of the membrane, protecting it from deposition of foulants. Ying and Ping (2006) reported a similar effect when dosing 0.75 and 1.5 g L^{-1} of PAC. Park *et al.* (1999) assumed that the solid and sharp-edged PAC works as a scouring agent that removes deposited foulants from the membrane surface when applied at 5 g L^{-1} in anaerobic MBRs. Adsorption of foulants to the PAC particles was mentioned by Fang *et al.* (2006) and Ng *et al.* (2006) as the responsible mechanism when dosing 2 - 5 g L^{-1} of PAC to activated sludge.

However, frequent refreshing of the PAC was necessary because PAC saturated with foulants and/or operation at an infinite SRT did exhibit a positive effect on filterability. A reduction of fouling explained by a stronger floc structure of sludge containing PAC was presented by Li *et al.* (2005) when using PAC at 1.2 g L^{-1} in an aerobic MBR and by Hu and Stuckey (2007) in an anaerobic MBR.

In pilot-scale aerobic MBR runs of more than 300 days with municipal wastewater, (reversible) cake-layer formation was found to be a negligible fouling mechanism (Remy *et al.*, 2009). Instead, membrane fouling dominantly consisted of the formation of a (irreversible) gel-layer, as was also described by Wang *et al.* (2008). In this paper we focus on the mechanism or combination of mechanisms responsible for the positive effect of PAC on the sludge filterability, with the emphasis on gel-layer formation. This knowledge can be used to fine-tune the PAC dose and to assess the possibility to apply an even cheaper additive.

5.2. Material and methods

5.2.1. Experimental set-up

Two identical pilot-scale MBRs (Figure 1), each with a total working volume of 85 L, were operated in parallel and fed with municipal wastewater for a period of 300 days. The wastewater was screened (5 mm) before entering the biological reactors. The COD of the wastewater was 350 mg L^{-1} on average, but fluctuated between 150 and 600 mg L^{-1}. The overall HRT of the MBRs was 10 hours. The oxygen concentration in the aerobic tank was measured on-line and controlled at 1.5 mg L^{-1} with a fine-bubble diffuser.

The membrane tanks were equipped with 2 homemade submerged PVDF flat sheet membranes with a nominal pore size of 0.1 µm and a surface area of 0.1 m^2 each. The channel width between the membranes was 6 mm. Coarse bubble aerators placed below the membranes provided a specific aeration demand (SAD) of 1.8 m^3 m^{-2} h^{-1} of air to scour the membrane surface and in this manner reduce fouling. With a peristaltic pump, permeate was extracted at a flux of 43.5 L m^{-2} h^{-1}.

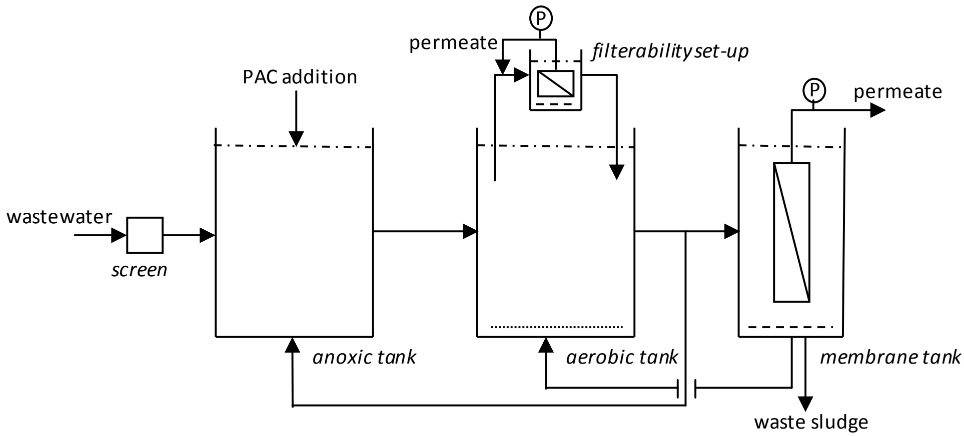


Figure 1 - *Pilot-scale MBR and set-up to measure filterability and critical flux.*

Both pilot reactors were operated at a SRT of 50 days. The average total suspended solid (TSS) concentrations respectively were 9.6 and 10.1 g L^{-1} in the aerobic tanks of MBRs without and with PAC addition. To achieve a PAC concentration of 0.5 g L^{-1} of sludge, in the set-up with PAC, 0.8 g of mesoporous Norit SAE Super PAC was added daily to the reactor to compensate the PAC wasted together with 1.6 L of sludge.

To measure sludge filterability, sludge from the aerobic reactors of the MBRs was continuously recirculated over a vessel with a volume of 5 L and a retention time of 1 hour (Figure 1). These vessels contained two flat-sheet PVDF submerged membranes, similar to the ones used in the pilot-plants, but with a much smaller surface area of 0.014 m^2. The filterability set-ups were equipped with a coarse bubble aerator to scour the membrane surface at a flow rate of 28 m^3 m^{-2} h^{-1}. This SAD is very high when compared to the SAD in the pilot-plant to compensate for the broad channel width and the relatively small surface area of the membranes used in these tests. The trans-membrane pressure (TMP) was monitored on-line, both in the pilot and in the filterability set-ups (Endress+Hauser, Cerebar M PMC 41).

5.2.2. Characteristics of the Powdered Carbons

The specific surface area, pore size and pore volume distribution of the PAC and of the non activated powdered carbon (PC) used for adsorption experiments, both provided by Norit Activated Carbon, were measured using nitrogen adsorption at -196 °C (liquid nitrogen temperature) with the Micromeritics Tristar 3000 and are given in Table 1.

	Unit	PAC	PC
Name		SAE Super	SA Super non activated
Raw material		Peat/wood	Peat/wood
Activation method		Steam	N/A
Mean particle diameter	µm	15	15
Surface	$m^2\ g^{-1}$	1360	335
Pore volume	$cm^3\ g^{-1}$	0.88	0.152
Average pore size	nm	2.6	1.82
Pores > 2nm	$m^2\ g^{-1}$	660	17

Table 1 - *Characteristics of the additives.*

5.2.3. Fractionation

Mixed-liquor supernatant was obtained with a centrifuge (Sigma, 2-16) at 3500 rpm for 15 minutes. After centrifugation, the supernatant was subsequently paper filtered (Whatman Black Ribbon 589/1, 12-25 µm) and membrane filtered (Cronus PTFE syringe filter, nominal pore size of 0.45 µm). The difference between paper and membrane filtrate will be referred to as the colloidal fraction and the membrane filtrate as the soluble fraction of the supernatant, respectively.

5.2.4. Chemical and physical analyses

Chemical Oxygen Demand (COD), and total suspended solids (TSS) were determined according to standard methods. Concentrations of polysaccharides and proteins were measured according to the methods of Dubois *et al.* (1956) and Bradford (1976), respectively using Glucose and Immunoglobulin G as standards. Cation concentrations were measured with ICP-OES (PekinElmer, Optima 5300DV). Biological Oxygen Demand (BOD) was determined with oxytop bottles (WTW, Weilheim, Germany), with a nitrification inhibitor (NTH 600, WTW).

Particle Size distributions (PSD) of the sludges and carbon particles were measured with Eyetech particle size analyzer in optic mode, coupled with an

Ankersmid liquid flow controller (LFC-101). Microscopic observations were performed with an inverted light-microscope (Leica DMI 6000B).

5.2.5. Scouring experiments

Batch tests were conducted to investigate the effect of virgin PAC particles on scouring of gel-layers which were formed on the membrane surface. Two gel layers were formed on the homemade PVDF membranes by filtration at a supra-critical flux of 100 L m^{-2} h^{-1} during fifty hours in the filterability set-ups (Figure 1), of sludges from the reactors with and without PAC. For both sludges this resulted in a TMP of more than 600 mbars and a visible gel layer. The filterability vessels were then emptied and refilled with permeate collected from the reactor operated with 0.5 g L^{-1} PAC addition. Filtration started at 50 L m^{-2} h^{-1} for 2 hours, then stopped and 0.5 g L^{-1} of (virgin) PAC was dosed to both filterability set-ups, and restarted at 50 L m^{-2} h^{-1} for 1.5 h, to check the effect of PAC on the TMP development as an indication for the scouring efficiency. Afterwards, the flux was decreased to 5 L m^{-2} h^{-1} for 1 hour to check the effect of PAC on TMP at low flux, to simulate a relaxation period also applied in the pilot-scale MBRs, before restarting filtration at 50 L m^{-2} h^{-1} for 1 hour.

5.2.6. Adsorption and degradation experiments

Mixed liquor from the reactor without PAC was mixed during one hour at 1600 rpm with a triple guarded blade and overhead mixer (Heidolph RZR2021) and then sonified (Branson sonifier 250, 200W) during two minutes to release proteins, polysaccharides and/or flocs fragments, which are all potential membrane foulants. The sonifier was used at a duty cycle of 50% (10 sec on, 10 sec off), for 2 minutes, with an output control of 20%. Centrifugation was applied to harvest the supernatant (Sigma, 2-16, 3500 rpm, 15 minutes). 350 mL erlenmeyers were filled with supernatant and additives, i.e. PAC at a concentration of 0.5 g L^{-1} or PC, also at a concentration of 0.5 g L^{-1}. They were placed on a shaker (Heidolph, Unimax 2010) at 150 rpm to keep the particles in suspension and at 4 °C to inhibit biodegradation as much as possible. Supernatant was sampled at the start of the experiment and after 24, 48 and 72 hours and analysed for soluble and colloidal COD, proteins and polysaccharides.

30 day BOD tests (BOD_{30}) were conducted in duplicate with the carbon particles collected at the end of the adsorption tests to determine the bioavailability of the foulants that were removed from the bulk. Both types of carbon particles were harvested from the previous tests by centrifugation (Sigma, 2-16, 3500 rpm, 15 minutes) and were resuspended in supernatant to a concentration of 0.5 g L^{-1}. To correct for supernatant BOD_{30}, a BOD_{30} test was also performed with supernatant without PAC or PC addition.

5.2.7. Shear experiments

Extra shear was applied to the sludge circulating over the filterability setup, with both sludges with and without PAC from the aerobic tanks of the pilot-scale MBRs. This extra shear was provided in the filterability set-up by an overhead mixer (Heidolph RZR2021) with a guarded triple bladed propeller at a rotation speed of 900 rpm. This corresponds to 800 s^{-1} of shear, considered as a standard for shear sensitivity determination (Mikkelsen & Keiding, 2002). Shear and recirculation already started 10 hours before the beginning of the filtration tests. The critical flux was determined, to assess the effect of shear on sludge filterability, using a flux-step method proposed by Van der Marel *et al.* (2009), consisting of cycles with 15 minutes permeation at a relatively high flux followed by 15 min relaxation at a low flux of 5 L m^{-2} h^{-1}. The flux was increased every consecutive cycle by 5 L m^{-2} h^{-1}, up to a maximum of 105 L m^{-2} h^{-1}. The critical flux was arbitrarily defined as the flux above which the rate of TMP increase exceeded 0.1 mbar min^{-1}. Supernatant quality (COD, polysaccharides, proteins and multivalent cations) was also followed, both in the filterability set-up where the extra shear was applied and in the aerobic tank of the pilot-scale MBR where it was circulated from.

5.3. Results

5.3.1. Scouring of the membranes

Figure 2 shows the average variations of TMP in time over 1 hour (dTMP/dt) during scouring tests by aeration in permeate and permeate with PAC. When starting filtration of permeate without PAC at 50 L m^{-2} h^{-1}, the TMPs were

104.3 mbar and 78.5 mbar, respectively for the membrane with the gel formed with the sludge without PAC and for the one with the gel formed with the sludge containing 0.5 g L^{-1} of PAC. In both cases filtration with permeate without PAC resulted in a positive dTMP/dt, probably due to further deposition of compounds present in the permeate or due to compression of the existing gels. This increase of filtration resistance shows that scouring by aeration alone does not result in a removal of the deposited gel on the membranes. Subsequent filtration of permeate containing 0.5 g L^{-1} PAC at 50 L m^{-2} h^{-1} for both gels resulted in a small negative average dTMP/dt of less than 0.01 mbar min^{-1}. The difference in TMP variation during this period when filtering permeate with and without PAC is possibly due to an effect of PAC, through an adsorption or flocculation/gluing to the PAC of the foulants present in permeate, avoiding their further deposition on the membrane. However, PAC does not seem to contribute significantly to gel removal because the negative dTMP/dt is very small.

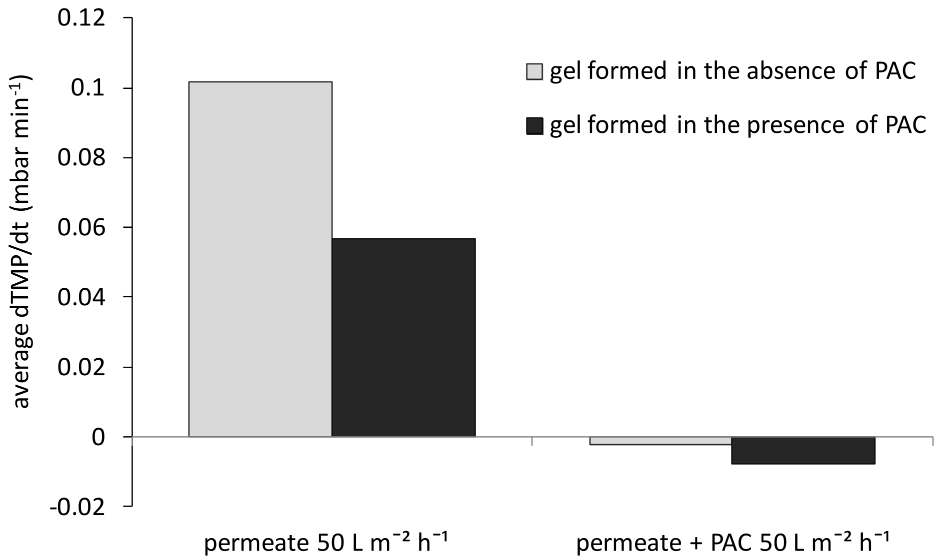


***Figure 2** - Average dTMP/dt during scouring tests.*

Filtration at a low flux of 5 L m^{-2} h^{-1} for 1 hour, while scouring with PAC, was also tested by comparing the stable TMP before and after this relaxation phase. This resulted in a low decrease of TMP with respectively 4.6 and 2.3 mbar for the gel formed in the absence of PAC and for the gel formed in the presence of PAC. This decrease was considered to be irrelevant because of the 1h of relaxation, as a much higher decrease in TMP would be necessary given the much shorter relaxation periods that are used in practice.

5.3.2. Adsorption and degradation of foulants

Figure 3 shows changes in colloidal and soluble COD during the adsorption tests with supernatant from the pilot-scale MBR in the presence of either PAC or PC. The results were similar for colloidal COD and 111 and 105 mg L^{-1} were removed from the supernatant after 72 hrs by PAC and PC, respectively. Apparently the removal of the "colloidal" COD fraction does not rely on adsorption but is caused by flocculation and therefore is independent from the pore size distribution of the carbon particles. This can also be seen from the microscopic images in figure 4; comparing individual PAC particles in demi water with PAC particles surrounded by flocculated material in the supernatant after 72 hrs of contact time. PAC particles are dispersed in demi water (Figure 4 a) while they aggregate when suspended in supernatant (Figure 4 b). As expected, the removal of soluble COD by PAC and PC showed a large difference with a maximum of 38 mg L^{-1} for PAC, already achieved within 24 hrs, but no significant removal of soluble COD with PC (Figure 3).

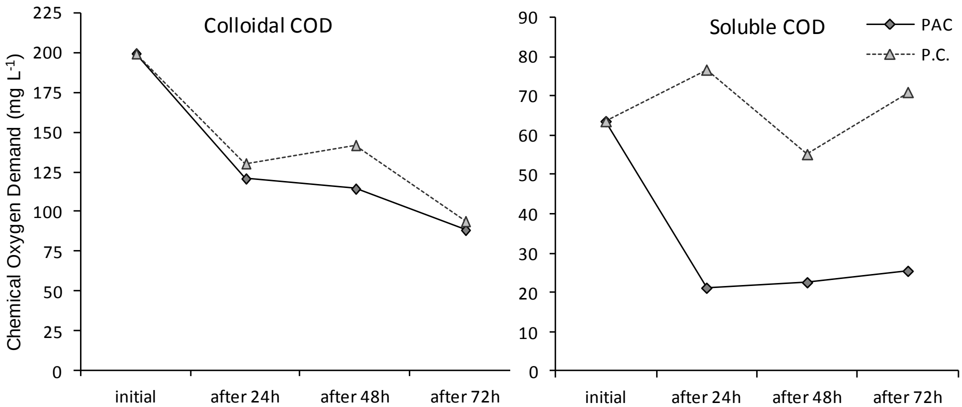
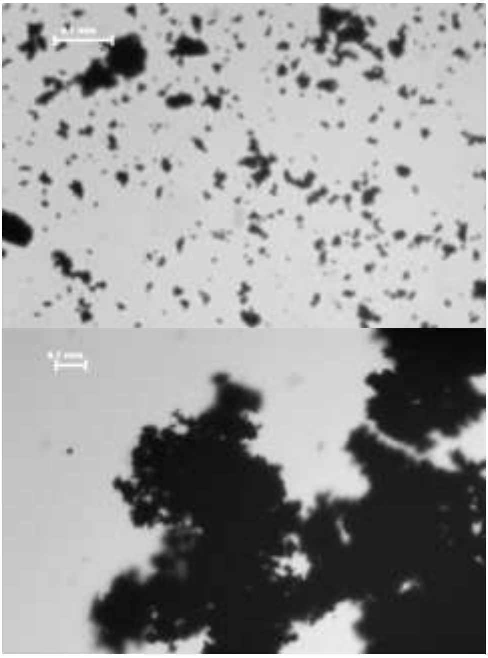


Figure 3 - *Colloidal and soluble COD during adsorption tests with activated (PAC) and non activated (PC).*



a. PAC in demi water b. PAC in supernatant

Figure 4 - *Microscopic observation of PAC particles.*

Table 2 shows the effect of 72 hrs contact time between supernatant with PAC and PC on the removal of COD, proteins and polysaccharides, the latter being suspected membrane foulants (Rosenberger *et al.*, 2006, Yigit *et al.*, 2008 and Drews *et al.*, 2008). Protein and polysaccharide removal showed similar behavior as COD, both for the colloidal and for the soluble fraction. Their removal efficiency however was considerably lower than for COD. Interestingly, polysaccharide removal was higher than protein removal with respect to the colloidal fraction, while it was the other way around for the soluble fraction. The latter is possibly due to the higher affinity of proteins to the PAC for adsorption, which was also found in adsorption tests with the model compounds, namely bovine serum albumin and glucose (data not shown).

	supernatant	removed with PAC		removed with PC	
	mg L^{-1}	mg L^{-1}	%	mg L^{-1}	%
colloidal					

COD	199	111	56	105	53
Proteins	28.3	8.2	29	6.8	24
polysaccharides	37.8	17.4	46	16.4	44
soluble					
COD	64	38	60	-7.4	-12
Proteins	8.0	4.2	53	0.9	11
polysaccharides	14.3	4.6	33	-2.6	-18

***Table 2 -** COD, proteins and polysaccharides removal with PAC and PC after 72 hrs of contact time with supernatant from the pilot-scale MBR.*

BOD_{30} concentrations, determined after the adsorption tests and already corrected for supernatant BOD_{30} in the absence of PAC or PC, were 76 and 97 mg O_2 L^{-1} for PAC and PC respectively. These concentrations already were corrected for a BOD_{30} of supernatant in the absence of PAC and PC of 47 mg L^{-1}. This implies that 51% of the colloidal and soluble COD that was removed by PAC during the adsorption test was biodegraded within 30 days. For the colloidal and soluble COD removed by PC this was close to 100%. This difference is most likely caused by the higher bioavailability of the COD loaded onto the outer surface of PC particles compared to a lower bioavailability of (soluble) COD adsorbed in the pores of the PAC particles.

Finally, adsorption of supernatant COD, proteins and polysaccharides also was determined for a much lower dose of virgin PAC of 4 mg L^{-1}, which corresponds to the PAC dose per liter of permeate. This however did not result in a detectable removal (data not shown). This means that adsorption alone cannot explain the removal of foulants from the supernatant

5.3.3. Floc strength

Figure 5 shows the course of the TMP during the critical flux determination with sludges without and with PAC addition, both submitted to additional shear in the filterability set-up. Sludge without PAC exhibited a higher increase of TMP than sludge with PAC. For sludge without PAC addition, a critical flux of 42.5 L m^{-2} h^{-1} was calculated, while sludge with PAC had a 19% higher critical flux of 50.6 L m^{-2} h^{-1}. In similar tests without extra shear, a 10% higher critical flux was found for sludge with PAC compared to sludge without PAC (Remy *et al.*, 2009).

The tests were duplicated after exchanging the membranes and the aerators to avoid biases due to the system and this gave similar results.

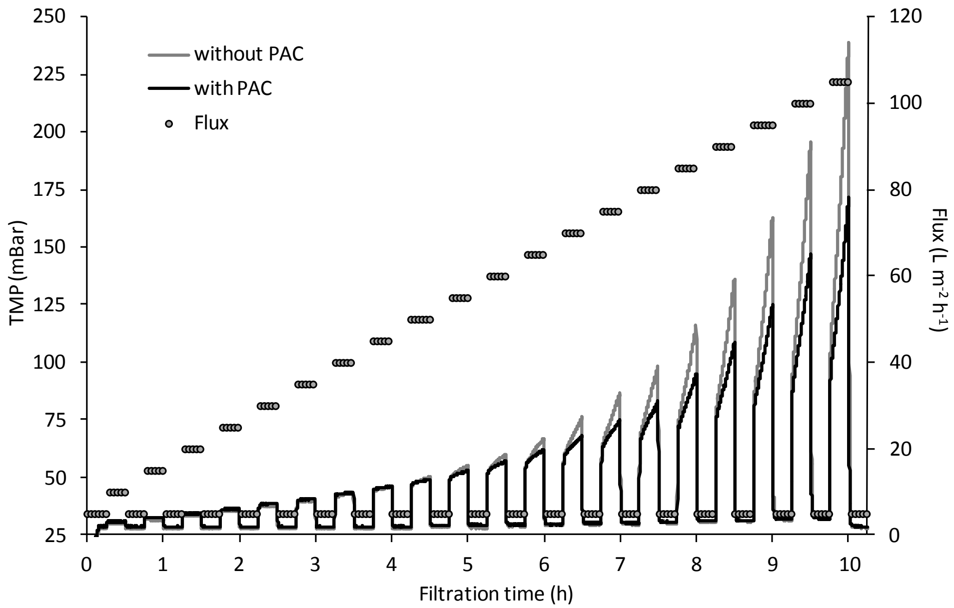


Figure 5 - *TMP during critical flux measurement with extra shear.*

Table 3 shows the effect of the extra shear on particle size of the sludges without and with PAC addition and COD, polysaccharides, proteins and the multivalent cations Ca^{2+} and Mg^{2+} concentrations in the supernatants of the sludges. Sludge from the (aerobic tank of the) pilot-scale MBR where no PAC was added showed only a slightly bigger particle size (72.2 µm) than the sludge from the (aerobic tank of the) pilot-scale MBR reactor where PAC was added (69.8 µm). The extra shear resulted in a much stronger reduction of the mean particles size of sludge without PAC (47.2 µm) than of sludge with PAC (67.5 µm).

Parameter		Sludge	no extra shear	extra shear	shear effect
Mean Diameter by volume (µm)		without PAC	72.2	47.2	- 34.6%
		with PAC	69.8	67.5	- 3.3%
Concentration in paper filtrate (mg L^{-1})	COD	without PAC	31.10	35.10	+ 12.9%
		with PAC	29.60	30.30	+ 2.4%
	Polysaccharides	without PAC	7.01	15.52	+ 121.4%
		with PAC	4.94	6.28	+ 27.1%
	Proteins	without PAC	9.60	10.35	+ 7.8%
		with PAC	8.76	10.29	+ 17.4%
Free multivalent cations (mg L^{-1})	Ca^{2+}	without PAC	67.1	72.2	+ 7.6%
		with PAC	70.6	71.3	+ 1.0%
	Mg^{2+}	without PAC	12.5	13.5	+ 8.0%
		with PAC	13.2	13.3	+ 0.8%

***Table 3 -** Effect of shear on mean particle diameter and supernatant concentrations of sludges without and with PAC addition in the aerobic tanks of the pilot-scale MBRs (no extra shear) and in the filterability set-up (extra shear).*

The extra shear also caused much higher increases of supernatant COD, polysaccharides and of the multivalent cations Ca^{2+} and Mg^{2+} for the sludge without PAC than for the sludge with PAC. For proteins however this was the other way around. This release of polysaccharides could explain the higher fouling, while the release of multivalent cations indicates floc disruption as multivalent cations are important for the structure of flocs (Sobeck & Higgins, 2002).

5.4. Discussion

Under the sub-critical flux conditions that were applied in the pilot-scale MBR (irreversible) gel-layer formation was found to be the dominant fouling mechanism. The formation of a protective PAC layer on the membrane surface therefore could be excluded as the mechanism for the reduced fouling that was observed in the presence of PAC.

The presence of PAC particles, while filtering permeate over a gel coated membrane, did not result in a significant decrease of the TMP, indicating that active removal of the gel-layer caused by scouring with the PAC particles did not take place. Moreover, in the sludge of the pilot-scale MBR all the PAC particles were incorporated in the sludge flocs and no free PAC particles were available to induce such a scouring effect. It cannot be excluded however that at much higher PAC concentrations than the 0.5 g L^{-1} applied in our experiments free PAC particles are available PAC aided scouring does occur.

Although soluble COD present in the permeate was adsorbed by PAC, subsequent biodegradation of this fraction did not take place. This implies that the PAC surface would become saturated with adsorbed COD and, in contrast to what was observed in the pilot-scale MBR, the positive effect of PAC on filterability would disappear. Adsorption of soluble COD by virgin PAC, followed by subsequent biodegradation therefore cannot explain why PAC helps to reduce membrane fouling. This was also confirmed by negligible differences in soluble concentrations of COD, proteins and polysaccharides in the supernatants of the pilot-scale MBRs operated with and without PAC (Remy *et al.*, 2012).

In the presence of virgin PAC it was shown that not only soluble COD but also colloidal COD was removed from the permeate. An improved flocculation of colloidal foulants therefore seems a more likely explanation as to why low concentrations of PAC reduce membrane fouling. However, similar to soluble compounds, no significant differences were observed in the colloidal concentrations of COD, proteins and polysaccharides between the pilot-scale MBRs operated with and without PAC, which also makes an improved flocculation of colloidal foulants not a likely explanation for the positive effect PAC had on sludge filterability.

When sludge from the pilot-scale MBRs was exposed to extra shear, sludge sampled from the pilot-plant with PAC exhibited a 19% higher critical flux than sludge sampled from the pilot-plant operated without PAC. Differences in the release of polysaccharides and COD, multivalent cations as well as the effect of the extra shear on the average floc size all indicated that the flocs with PAC were more shear resistant than flocs without PAC. Not only are polysaccharides suspected membrane foulants (Rosenberger *et al.*, 2006, Yigit *et al.*, 2008 and

Drews *et al.*, 2008) but together with the multivalent cations they are important for a strong floc structure (Urbain *et al.*, 1993, Biggs & Lant, 2001 and Sobeck & Higgins, 2002). This strength is particularly important in the vicinity of the membrane surface where the flocs are exposed to extra shear. It can therefore be expected that strong sludge flocs with incorporated PAC will release less foulants and cause less gel layer formation than weaker flocs without PAC.

From the above it can also be concluded that cheaper particles such as PC, or even PAC previously used for post-treatment may be used as an even cheaper alternative for PAC to reduce membrane fouling in MBRs. Initially, PAC was selected as it may have the additional benefit of an improved micropollutant removal, which has become a serious issue over the last decade. It still needs to be investigated whether this really is the case at the low PAC dosages that were applied in this research.

5.5. Conclusions

Several mechanisms which can explain the positive effect of a low PAC dosage on sludge filterability were investigated. An enhanced membrane scouring or adsorption of membrane foulants could not explain this positive effect. Instead, the formation of stronger sludge flocs in the presence of PAC and therefore a higher shear resistance and lower release of foulants in the vicinity was demonstrated to be the most likely explanation. The same effect may also be achieved by cheaper alternatives for PAC.

5.6. Acknowledgement

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Chapter 6. EFFECT OF LOW DOSAGES OF POWDERED ACTIVATED CARBON ON MBR PERFORMANCE

Maxime Remy[1,2], Hardy Temmink[1,2] Wim Rulkens[2]

[1.] Wetsus, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

[2.] Wageningen University, Sub-department of Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

Abstract - Previous research demonstrated that powdered activated carbon (PAC), when applied at very low dosages and long SRTs, reduces membrane fouling in membrane bioreactors (MBRs). This effect was related to the formation of stronger sludge flocs, which are less sensitive to shear. In this contribution the long-term effect of PAC addition was studied by running 2 parallel MBRs on sewage. To one of these, PAC was dosed and a lower fouling tendency of the sludge was verified, with a 70% longer sustainable filtration time. Low PAC dosages showed additional advantages with regard to oxygen transfer and dewaterability, which may provide savings on operational costs.

Keywords - membrane fouling; membrane bioreactor; powdered activated carbon; sludge characteristics; filterability

Remy, M., Temmink, H. and Rulkens, W. (2012), Effect of low dosages of powdered activated carbon on membrane bioreactor performance, Water Science & Technology, Vol. 65 (5), pp. 954-961.

6.1. Introduction

Membrane bioreactors (MBRs) have a 30 to 50% higher energy consumption than conventional wastewater treatment plants employing secondary settlers. This is mainly caused by the necessity to prevent excessive membrane fouling. In the case of sewage treatment this is the main bottleneck for a more widespread application of MBR technology, even though this technology offers advantages such as smaller footprint, improved effluent quality and better possibilities to reuse the effluent (Judd, 2006).

Research to reduce membrane fouling mainly focuses on optimizing membrane materials (e.g. Van der Marel *et al.*, 2010), improving membrane module design and membrane operation (Meng *et al.*, 2009), and, to a lower extent, on enhancing the filterability of the feed sludge by additives such as organic and inorganic flocculants and powdered activated carbon (PAC) (e.g. Koseoglu *et al.*, 2008 and Ying & Ping, 2006). For example, in short-term experiments Remy *et al.* (2009) demonstrated that very low PAC dosages of 0.5 g L^{-1} of sludge, corresponding to 4 mg PAC L^{-1} of wastewater, already can significantly improve sludge filterability. The critical flux in the presence of PAC was found to be 102 L m^{-2} h^{-1}, which was 11% higher than a critical flux of 92 L m^{-2} h^{-1} in the absence of PAC. Also much longer periods could be sustained without significant fouling. Further research by Remy *et al.* (2010) strongly indicated that this positive effect of PAC could be attributed to the formation of stronger sludge flocs, as was demonstrated under conditions of enhanced shear by a lower release of potential membrane foulants from the sludge flocs and a smaller decrease of the floc size compared to sludge without PAC.

In this paper the effect of similar low PAC dosages on long-term fouling behavior and on sewage treatment performance was studied in a pilot-scale MBR during a period of almost a year. This was compared to a reference MBR without PAC addition. Because PAC changes the structure of the sludge flocs, it was expected that also other important performance parameters such as oxygen transfer efficiency and sludge dewaterability could be affected. Both are important parameters for the energy efficiency of wastewater treatment plants. Therefore, these parameters were also compared for sludges taken from the two MBR systems. Finally, an important topic for the near future with respect to receiving surface water quality is the removal of organic micropollutants. To investigate a potential additional advantage of PAC addition on this removal both MBRs were spiked with a number of selected micropollutants.

6.2. Material and Methods

6.2.1. Pilot-scale MBRs and operation

Two identical pilot-scale MBRs, each with a total working volume of 85 L, were operated in parallel and fed with sewage. Figure 1 is a schematic representation of the two pilot-scale MBRs. The total hydraulic retention time (HRT) was 10 h, with 4.1 h anoxic retention time to accommodate denitrification, 4.1 h aerobic retention time and 1.8 h retention time in the membrane tank. Both MBRs were operated at a sludge retention time (SRT) of 50 days. The dissolved oxygen concentration in the aerobic tank was maintained at 1.5 mg L^{-1} using a fine-bubble diffuser (ITT Flygt, Sanitaire 9” membrane). Further details about the pilot-scale MBRs can be found in Remy *et al.* (2009).

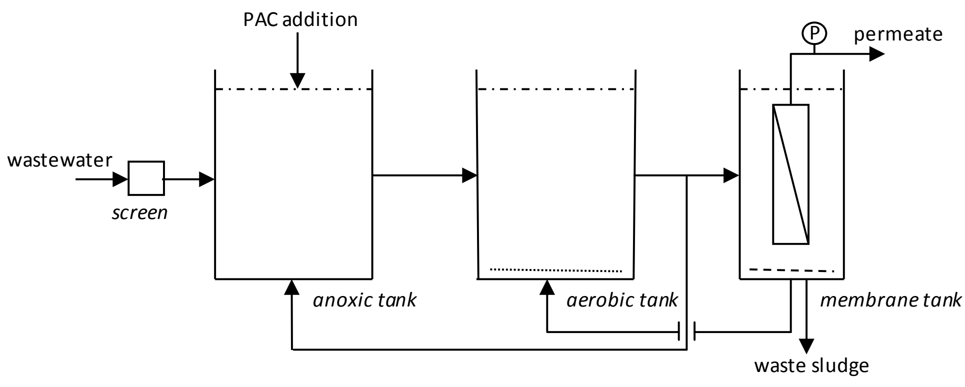

***Figure 1 -** Schematic representation of the pilot-scale MBR.*

The membrane tanks were equipped with homemade double-sided submerged PVDF flat sheet membranes with a nominal pore size of 0.1 µm and a surface area of 0.1 m^2 each. The channel width between the membranes was 6 mm. Coarse bubble aerators located below the membrane sheets provided a specific aeration of 1.8 m^3 m^{-2} h^{-1}. Trans membrane pressure (TMP) was monitored on-line and registered continuously (Endress+Hauser, Cerebar M PMC 41). Membrane cleaning was performed as soon as the TMP exceeded 75 mbar. The cleaning procedure consisted of gentle rinsing with permeate using a nozzle to remove gel layer deposition, rinsing with demineralized water, soaking in 3000 ppm sodium hypochlorite for 2 hours followed by 1 hour in 1% oxalic acid and once more rinsing with demineralized water. Initially, the membrane flux was set at 43.5 L m^{-2} h^{-1}, later on the flux was increased to 58 and 87 L m^{-2} h^{-1}. Those fluxes were respectively used for periods of 280, 35 and 5 days. To avoid changes in the HRT, increase of flux was accomplished by taking out membrane sheets, keeping the flow over the reactor stable.

The MBRs were fed with sewage for a total period of 320 days. The sewage passed a 5 mm sieve, followed by a grit removal unit. The average sewage composition, based on weekly samples, was 353 $\pm$ 190 mg COD L^{-1} and 54 $\pm$ 14 mg NH_4^+-N L^{-1}. The COD consisted of 70% suspended solids, 12% colloidal material and 18% soluble material. Daily, 0.8 g of mesoporous PAC (Norit SAE Super) was added to the anoxic tank of one of the two MBRs to compensate for the amount of PAC that was wasted with the excess sludge. This corresponds to a concentration of 0.5 g PAC L^{-1} of sludge and a dosage of 4 mg PAC L^{-1} of wastewater. More background information on the PAC characteristics can be found in Schouten *et al.* (2007).

Seven different organic micropollutants (Table 1) were continuously dosed to the wastewater to reach a concentration of 5 µg L^{-1} of sewage during a period of 100 hours, i.e. 10 times the HRT. A stock solution containing 2.175 mg L^{-1} of each micro-pollutant and 10 ppm methanol in demineralized water was used for this purpose. More background information on these micro-pollutants can be found in the work by Hernández (2010).

Compound	Abbreviation	Application
2-phenyl-5-benzimidazolesulfonic acid	PBSA	UV filter
caffeine	-	stimulant
bisphenol A diglycidyl ether	BADGE	plasticizer
bisphenol F diglycidyl ether	BFDGE	plasticizer
benzalkonium chloride	BaCl	surfactant
benzophenone-3	BP-3	UV filter
butyl methoxydibenzolymethane	Avobenzone	UV filter

Table 1 - *Spiked organic micro-pollutants.*

6.2.2. Sampling and chemical analyses

Grab samples of wastewater, supernatant fractions from the membrane tank mixed liquor and of permeate were taken on a weekly basis. Supernatant from the membrane tank mixed liquor was obtained with a centrifuge (Sigma, 2-16), operated for 15 minutes at 3000 rpm, corresponding to 1500 g. The supernatant was sequentially paper filtered (Whatman Black Ribbon 589/1) and filtered with a PTFE 0.45 µm pore size membrane filter (Cronus). The difference between paper and membrane filtrate is referred to as the colloidal fraction of the supernatant, and the membrane filtrate as the soluble fraction. COD as well as total suspended solids (TSS) and volatile suspended solids (VSS) of sludge samples were all determined according to standard methods (APHA-AWWA-WEF, 1998). Micro-pollutant concentrations in the permeate were determined according to analytical methods described by Hernández *et al.* (2010).

Concentrations of polysaccharides and proteins were determined according to methods of Dubois *et al.* (1956) using glucose as the standard and Bradford (1976) using immunoglobulin as the standard, respectively. Extracellular polymeric substances (EPS) bound to the sludge flocs were extracted by mixing the sludge with cation exchange resin, using a method adapted from Frølund *et al.* (1996). To remove similar EPS compounds from bulk water, first a washing step was performed on the sludge. The sludge was centrifuged at 2000 g for 15 min. Sludge pellets were resuspended to their original volume using a buffer consisting of 2 mM Na_3PO_4, 4 mM NaH_2PO_4, 9 mM NaCl and 1 mM KCl at pH 7. The EPS extraction was performed as follows: 300 mL sludge was transferred to a beaker and the cation exchange resin (DOWEX® Marathon® C, Na^+ form, with 70 g g_{VS}^{-1}) was added. The suspension was stirred at 900 rpm for 4 hours at 4 °C. The extracted EPS were harvested by centrifugation following the fractionation method presented above after which COD, polysaccharides and proteins were determined. Dissolved organic carbons (DOC) from the permeates were measured with LC-OCD (Liquid Chromatography - Organic Carbon Detection) by D.O.C Labor (Germany).

6.2.3. Sludge parameters

Dynamic viscosity of sludge samples was assessed at 20 °C, with a HAAKE rotary viscotester 6L using spindle L1 at different rotational speeds (0 - 200 rpm). Settleability of sludge samples, expressed as the sludge volume index (SVI) was measured according to standard methods (APHA-AWWA-WEF, 1998) after diluting the sludge 4 times in permeate. Particle size distribution of the sludge was measured with an Eyetech particle size analyzer, with a range from 5 till 600 µm, and using video measurements coupled with an Ankersmid liquid flow controller LFC-101. Oxygen transfer parameters (k_La and respiration rate) from sludge samples were determined in non steady-state batch tests under endogenous respiration conditions, following the method described by WEF & ASCE (2001). Three liters beakers were used and several air flow rates were applied. The beakers were mixed with a Heidolph overhead mixer at 400 rpm. The temperature of the sludge was kept constant at 20 °C. During those tests, the dry solids concentrations were 9.8 and 10.3 g L^{-1}. Dissolved oxygen concentration was followed in time by a HACH handheld DO meter.

6.3. Results

6.3.1. Membrane fouling

Membrane cleaning was performed as soon as a TMP exceeded 75 mbar. Long-term operation at the initial flux of 43.5 L m^{-2} h^{-1} showed that for the MBR with PAC addition a much lower cleaning frequency was required than for the MBR without PAC addition. The average sustainable filtration time, i.e. the average operational period between two cleanings, was 55 days for the system with PAC and 32 days for the system without PAC. This represents an increase of sustainable filtration time of over 70%. Remarkably, during periods of low sewage temperatures, typically below 12 °C, sludge foaming, associated with membrane fouling by You and Sue (2009), was frequently detected in the MBR without PAC addition whereas foaming did not occur in the MBR with PAC.

Figure 2 illustrates for three representative periods the effect of the different membrane fluxes on the TMP development in the two MBR systems. At a flux of 43.5 L m^{-2} h^{-1}, even after 10 days after the last cleaning procedure, neither MBR exhibited significant fouling. A higher flux of 58 L m^{-2} h^{-1} in the MBR without PAC addition resulted in a severe increase in TMP and required frequent cleaning actions (Figure 2). At the same flux, in the MBR with PAC addition the TMP increase was below 5 mbar for the 10 days. At the highest flux of 87 L m^{-2} h^{-1} severe fouling was detected in both MBRs, although the required cleaning frequency was rather significantly lower for the MBR with PAC addition.

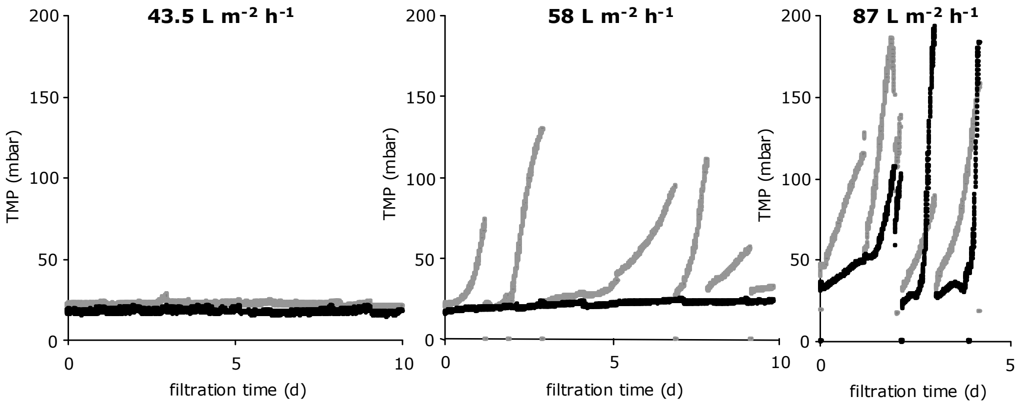

Figure 2 *-TMP development in the MBRs with (black lines) and without PAC addition (grey lines) during representative periods at membrane fluxes of 43, 58 & 87 L m^{-2} h^{-1}.*

Visible gel deposition on the membrane surface took place in both MBRs. However, the gel layer in the MBR with PAC addition was much easier to remove, as indicated by the distance between the nozzle and the membrane surface required for rinsing, i.e. 15 cm compared to 7 cm for the gel that deposited in the system without PAC addition. On one occasion, gel deposition was investigated after running new membranes during 12 hours at 90 L m^{-2} h^{-1}. The TMP for sludge without PAC was 600 mbar and the one for sludge with PAC was 300 mbar.

Parameter	MBR without PAC (g m^{-2})	MBR with PAC (g m^{-2})
COD	409	191
polysaccharides	93	32
proteins	67	26
ratio proteins/polysaccharides	0.72	0.82

***Table 2 -** Composition of the gel layer harvested from the membranes after operating during 12 hours at a flux of 90 L m^{-2} h^{-1}.*

The gels were harvested and homogenized by sonication and their COD, polysaccharide and protein composition was determined (Table 2). Clearly, the gels from the MBR with PAC addition contained much lower amounts of organic material than the gels which were harvested from the MBR without PAC addition. Also, the protein to polysaccharide ratio of the gel was lower (0.72) than in the MBR with PAC (0.82).

6.3.2. Treatment performance

Average COD, polysaccharide and protein concentrations in the membrane tank supernatant and permeate over a period of 320 days are given in Table 3. Average COD removal efficiencies were 88% and 89% for the MBR without and with PAC, respectively. LC-OCD measurements of the permeate showed that the DOC in the permeate of both reactors consisted mostly of poorly biodegradable humic substances, probably already present in the sewage that was treated (Huck, 1999). Although the differences were small and exhibited considerable variation in time, for all three mentioned parameters the concentrations in the supernatant of the membrane tank and in the permeate were consistently lower in the MBR system with PAC than in the MBR system without PAC. For over 90% of the simultaneous samplings, the permeate from the reactor with PAC showed lower concentrations when compared to the one of the reactor without PAC. Membrane rejection with respect to COD, polysaccharides and proteins are also presented in Table 3. These were similar for the two MBRs, apart from the polysaccharide rejection of 11% in the MBR with PAC, which was considerably lower than polysaccharide rejection of 18% in the system without PAC. This corresponds with the higher protein to polysaccharide ratio in the gel layer which deposited on the membrane surface in the MBR with PAC (Table 2).

Parameter	MBR without PAC			MBR with PAC		
	supernatant	permeate	rejection	supernatant	permeate	rejection
COD	43	33.3	22	40	31.4	22
polysaccharides	8.7	7.2	18	7.8	6.9	11
proteins	4.8	3.6	23	4.3	3.1	28
ratio prot/poly	0.55			0.55		

Table 3 - *Average membrane tank supernatant and permeate concentrations of COD, polysaccharides and proteins and membrane rejection of these compounds (concentrations in mg L^{-1} and rejection in %).*

Figure 3 compares the removal efficiencies of the selected organic micropollutants for the two MBR systems. They were all removed with a decreasing efficiency in the order: caffeine > BP-3 > BADGE > avobenzone > BFDGE > BaCl > PBSA. Removal efficiencies were in the same range as what was observed by Hernández *et al.* (2010) in an aerobic biological grey water treatment reactor, and can be explained by biodegradation (caffeine, BADGE, BFDGE) or adsorption to the biological sludge (BP-3, avobenzone, BaCl). However, in the study by Hernández (2010) PBSA was not removed biologically but could be removed by adsorption to PAC. For all compounds, apart from caffeine which in both MBRs was completely removed, the removal efficiency in the system with PAC was slightly higher than in the MBR without PAC, indicating an enhanced adsorption capacity caused by the sludge with PAC particles. For PBSA the difference in removal efficiency between the two MBRs was more substantial than for the other compounds.

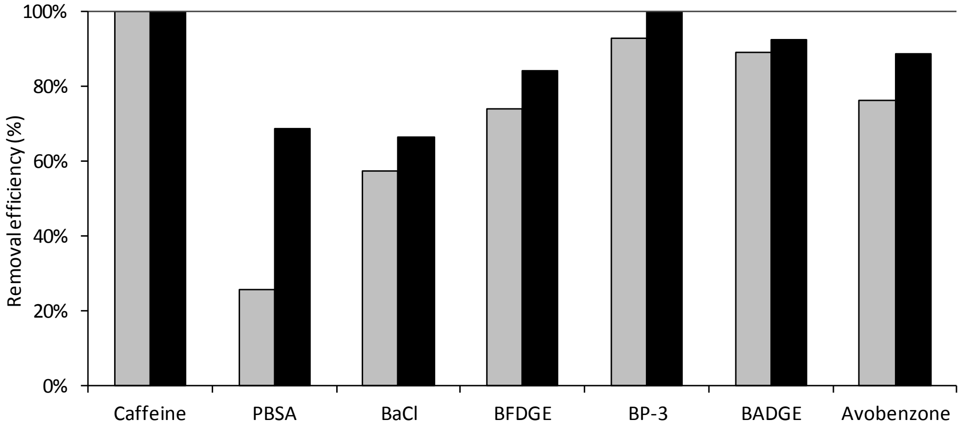

Figure 3 - *Removal efficiencies for selected organic micro-pollutants in MBR without PAC (grey bars) and with PAC (black bars).*

6.3.3. Sludge properties

Average suspended solids concentration in the MBR systems without and with PAC were 9.6 ± 0.9 and 10.1 ± 1.3 g L^{-1} respectively, with volatile fractions of 76 and 78%. These differences can be completely attributed to the presence of PAC. Concentrations of extracellular polymers extracted from sludge samples are presented in Table 4. Based on COD, the amount of extracted extracellular polymers was significantly higher in the MBR without PAC. Differences between the two MBR systems in extracted polysaccharides and proteins are small, but the ratios extracted proteins to extracted polysaccharides (0.73 and 0.84 respectively for the MBR sludge without PAC and the MBR sludge with PAC) correspond very well with the protein to polysaccharides ratios that were found in the gel layers that deposited on the membrane surfaces (Table 2).

Parameter	MBR without PAC mg g VSS^{-1}	MBR with PAC mg g VSS^{-1}
COD	164	127
polysaccharides	31	27
proteins	23	22
ratio proteins/polysaccharides	0.73	0.84

Table 4 - *Concentration of extracted polymeric substances.*

The average equivalent area diameter of the particles respectively was 65.1 and 72.2 µm for sludge taken from the MBR without PAC and the MBR with PAC. The particle size distribution (data not shown) did not exhibit a peak at 15 µm, which is the average size of the PAC particles. This implies that the PAC particles were incorporated in the sludge flocs, which was also confirmed by microscopic sludge observations (data not shown).

Because the PAC amended sludge had a slightly higher suspended solids concentrations than the sludge without PAC (10.1 compared to 9.6 g L^{-1}), a higher (apparent) dynamic viscosity was expected (e.g. Seyssiecq *et al.*, 2008). However, Figure 4 clearly demonstrates that at the lower shear speed (rpm), the sludge with PAC is less viscous than the sludge without PAC. In addition, the PAC amended sludge is less shear-thinning, which indicates it is more resistant to shear.

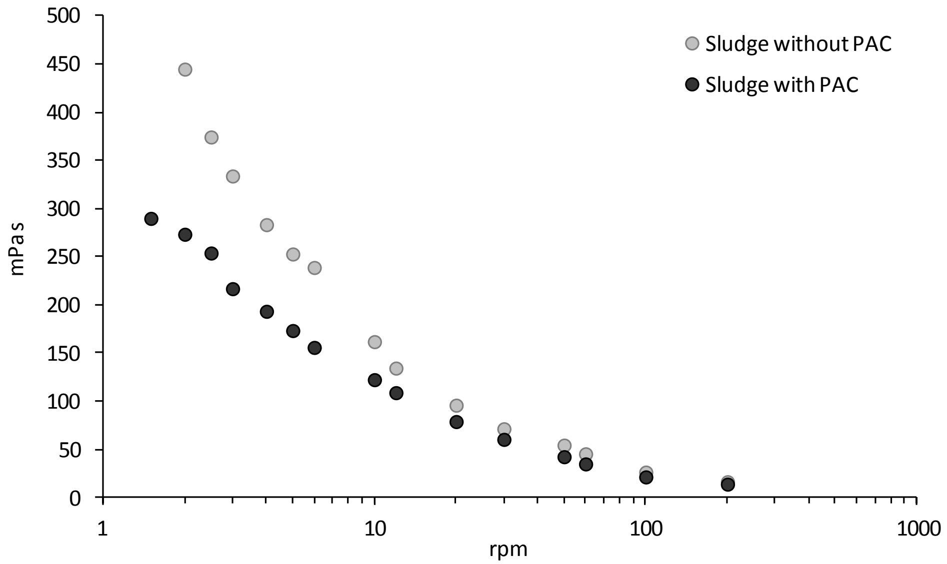

Figure 4 - *Apparent dynamic viscosity of the sludge with and without PAC.*

The oxygen transfer efficiency k_La of both sludges was determined at four different air flow rates. On average, the k_La of the sludge with PAC was found to be consistently higher than of the sludge without PAC with an average difference of 11% while no difference could be found in the respiration rate. The differences in k_La are probably related to the lower dynamic viscosity of the sludge with PAC than the sludge without PAC (Figure 4) (Germain & Stephenson, 2005).

Although not directly relevant for MBRs, the sludge volume index (SVI) as a measurement of settleability of the MBR sludges was determined as an indication for their dewaterability (Li & Yang, 2007). The SVI of the sludge without PAC was 150 mL g^{-1} while the SVI of the sludge with PAC was 45% lower, i.e. 80 mL g^{-1}.

6.4. Discussion

Short-term filtration experiments with PAC amended sludge had demonstrated that PAC already at very low dosages reduces the membrane fouling potential of the sludge mixture (Remy *et al.*, 2009). Further investigations strongly indicated this lower fouling potential is not caused by an enhanced scouring of the membrane surface with PAC particles or to adsorption of potential membrane foulants such as polysaccharides and proteins, but most likely is caused by the formation of stronger activated sludge flocs, which have a higher resistance to shear (Remy *et al.*, 2010). In this study the positive effect of low concentrations of PAC was confirmed during long-term operation of a MBR. Supernatant composition in the membrane tank mixed-liquor was not very different from the composition in the reference MBR without PAC addition. However, some differences were observed. Less organic material deposited as a gel layer on the membrane surface in the MBR where PAC was dosed. The ratio between proteins and polysaccharides in the gel layer that formed with PAC amended sludge was higher than in the MBR without PAC addition and, in both MBRs this ratio corresponded very well with the protein to polysaccharide ratio of the extracellular polymers that could be extracted from the sludge. Possibly, due to the enhanced shear in the vicinity of the membrane surface, in the case of sludge without PAC addition more of the bound extracellular polymers are loosened from the floc structure and become membrane foulants. This in particular applies to polysaccharides, which also by others have been reported to be the most important membrane foulants (e.g. Rosenberger *et al.*, 2006, Yigit *et al.*, 2008 and Drews *et al.*, 2008).

Long-term MBR operation at different fluxes showed that a low dosage of PAC makes it possible to operate MBRs at significantly higher fluxes. In our experiments it was possibly to increase the flux from 43.5 to 58 L m^{-2} h^{-1} without any fouling problems, whereas in the system without PAC addition this resulted in a dramatic increase of the cleaning frequency. Such a 33% increase of the sustainable flux has a large impact on the energy consumption of MBR systems because it implies that less membrane surface area can be installed with a lower energy consumption to scour this membrane surface.

Another observation was an 11% higher k_La of the PAC amended sludge. Because together with air scouring of the membranes oxygen transfer in MBRs is the biggest energy consuming process, this further contributes to a lower overall energy consumption of MBRs.

Treatment performance of the MBR with PAC addition was not very different from the MBR which was operated without PAC, although consistently lower effluent concentrations were observed with respect to COD. A number of selected organic micropollutants were removed at a slightly higher efficiency, probably due to additional adsorption to the PAC particles. But, apart from the additional removal of the UV filter PBSA, the differences were not large enough to justify the addition of PAC. Apparently the dosage of 4 mg PAC L^{-1} of wastewater (0.5 g PAC L^{-1} of sludge) was too low to accommodate a complete removal of the selected organic micropollutants, even though Hernández (2010) showed that this objective can be achieved by activated carbon treatment.

The MBR sludge with PAC exhibited a much better settleability than MBR sludge without PAC: SVI values of 80 compared to 150 mL g^{-1}. Although not directly related, a better settleability is an indication of a higher sludge dewaterability (Li & Yang, 2007), which may have important implications for the sludge treatment equipment and costs. A similar positive effect of PAC on sludge dewaterability was also reported by Çeçen *et al.* (2003) and, according to Yang and Li (2009) may be caused by the lower amount of (loosely) bound extracellular polymers in the PAC enriched sludge (Table 4).

Considering the low costs of PAC addition of less than 0.01 euro per cubic meter of permeate, and the large potential advantages this gives with respect to fouling, energy consumption and dewaterability as outlined above, PAC addition is a good strategy for sewage treatment by MBRs.

6.5. Conclusions

The effect of PAC was investigated over a period of 320 days in two pilot-scale MBRs treating municipal wastewater. It was shown that the combination of a low PAC dosage (0.5 g L^{-1} of sludge) combined with a relatively long SRT of 50 days resulted in:

- an improvement of the sustainable filtration time of 70%,
- a possibility to increase the sustainable flux by at least 30%,
- a slight but consistent improvement of the permeate quality,
- an increase of the oxygen transfer by 11%,
- a probable increase of the dewaterability as indicated by a 45% lower SVI,
- an increased efficiency regarding the removal of organic micro-pollutants.

6.6. Acknowledgements

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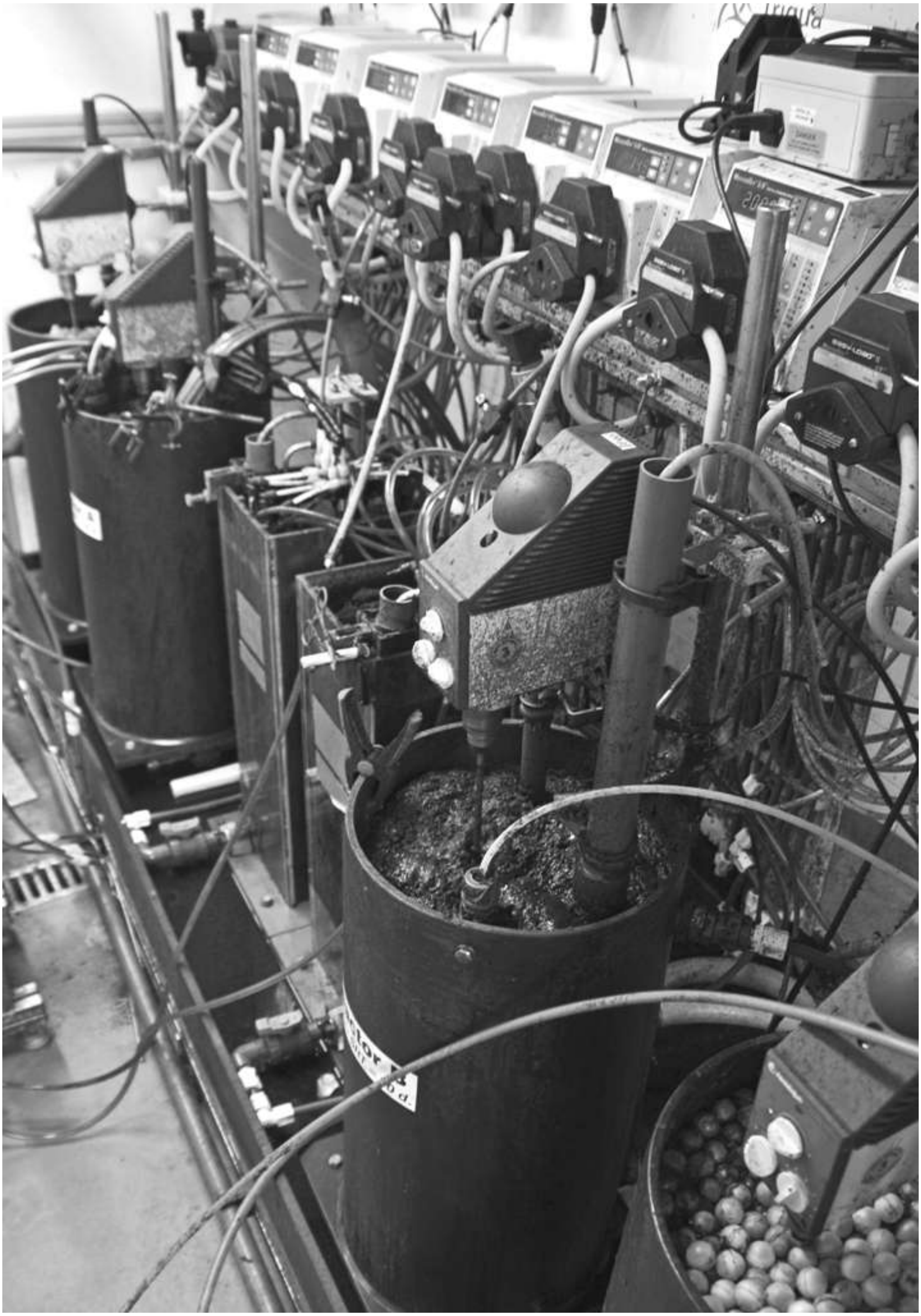

Chapter 7. LOW POWDERED ACTIVATED CARBON CONCENTRATIONS TO IMPROVE MBR SLUDGE FILTERABILITY AT HIGH SALINITY AND LOW TEMPERATURE

Maxime Remy[1,2], Hardy Temmink[1,2], Paula Van den Brink[1,3] and Wim Rulkens[2]

[1.] Wetsus, P.O. Box 1113, 8900 CC Leeuwarden, The Netherlands

[2.] Wageningen University, Sub-department of Environmental Technology, P.O. Box 17, 6700 AA, Wageningen, The Netherlands

[3.] Delft University of Technology, Department of Biotechnology, Julianalaan 67, 2628 BC Delft, Netherlands

Abstract - Previous research has demonstrated that powdered activated carbon (PAC), when applied at very low dosages and long SRTs, reduces membrane fouling in membrane bioreactor (MBRs). This effect was related to stronger flocs which are less sensitive to shear. Low temperature and high salt concentration are known to drastically decrease the filterability of the sludge. In this paper the effect of PAC addition on the robustness of MBR when submitted to these disrupting conditions was investigated. PAC amended sludge showed a higher resistance to high salinity with a lower fouling development and release of foulants. When submitted to lower temperatures, the sludge without PAC showed a clear decrease of the filterability, while the filterability of PAC amended sludge was much less affected. PAC addition does not only improve the filterability in the MBR under normal conditions but also when the sludge is submitted to stress. A low PAC dosage could be used during startup and difficult conditions (e.g. winter) to minimize detrimental effects of such conditions.

Keywords - membrane fouling; membrane bioreactor; powdered activated carbon; salinity; temperature

Remy, M., Temmink, H., Van den Brink, P. and Rulkens W. (2011), Low powdered activated carbon concentrations to improve MBR sludge filterability at high salinity and low temperature, Desalination, Vol. 276, pp. 403-407.

7.1. Introduction

Membrane bioreactors (MBRs) offer several advantages compared to conventional activated sludge systems (CAS), including a smaller footprint and a better effluent quality. Nevertheless, their application is often hampered by membrane fouling, which results in higher energy consumption and operational costs compared to CAS, and by their higher sensitivity to changes in environmental and operational conditions (Judd, 2006 and Drews, 2010). Two important parameters with a negative effect on sludge filterability are elevated levels of monovalent cations and a low wastewater temperature.

High concentrations of monovalent cations such as Na^+ have a detrimental effect on sludge flocculation and settleability (Sobeck & Higgins, 2002 and Biggs *et al.*, 2001). Floc strength is partly determined by extracellular polymers (EPS) that are responsible to maintain the floc structure and by divalent cations such as Ca^{2+}, forming bridges between the polymers. At high concentrations the divalent cations can be replaced by monovalent cations, causing weaker intrapolymer bridges, and flocs that are more sensitive to shear. Under these conditions it can be expected that more EPS will be released from the sludge flocs to the bulk liquid and, as they are known membrane foulants (Wang *et al.*, 2009), this will cause a deteriorating sludge filterability. Reid *et al.* (2006) observed a negative effect of salt shocks (Na^+ and K^+) on sludge filterability, and related this mainly to the release of polysaccharides. This effect is most evident at very high monovalent cation concentrations, for example for shipboard wastewater containing 30 g L^{-1} of salt (Sun *et al.*, 2010 and Lay *et al.*, 2010). However, Song and Singh (2005) observed that monovalent cation concentrations as low as 5-20 mM already caused and enhanced release of membrane foulants. Saline wastewaters are produced by the industry, e.g. food, petroleum, textile and leather (Lefebvre & Moletta, 2006) and improving the robustness of MBRs to treat these types of wastewaters would extend the fields of their application.

A lower treatment performance of CAS at lower temperatures, both in terms of conversion rates and sludge settleability, is well known (McClintock *et al.*, 1993, Lishman *et al.*, 2000 and Wilén *et al.*, 2000). For MBRs, Chiemchaisri and Yamamoto (1994) reported that a lower temperature resulted in a dramatic decrease of filterability and permeate quality. Also Lyko *et al.* (2008), who followed membrane performance in a MBR over a period of two years, observed a detrimental effect of low temperatures. Although a lower filterability partly can be explained by a higher viscosity (Fan *et al.*, 2006), filterability at lower temperatures generally is much lower than what can be expected based on a higher viscosity alone, indicating an enhanced fouling (Jiang *et al.*, 2005). This can be explained by (1) a decrease of membrane surface scouring due to a lower shear stress if coarse bubbles are applied, (2) stronger deflocculation of the sludge and (3) a lower degree of biodegradation of wastewater pollutants, including potential membrane foulants (Le-Clech *et al.*, 2006). Rosenberger *et al.* (2006) and Drews *et al.* (2008) related the increased fouling at low temperatures to higher levels of polysaccharides in the supernatant of the sludge.

Previous research demonstrated the positive effect of low dosages of powdered activated carbon (PAC) on sludge filterability (Remy *et al.*, 2009 and Remy *et al.*, 2012), even at dosages as low as 0.5 g L^{-1} of sludge. When combined with long sludge retention times (50 days) the addition corresponds to 4 mg of PAC per liter of treated wastewater, which result in estimated additional costs of only 0.008 € m^{-3} of wastewater. Remy *et al.* (2010) demonstrated that the improved filterability was caused by an enhanced strength of the sludge flocs in the presence of PAC. In this contribution it was explored whether low dosages of PAC can also help to counteract the negative effects of low temperatures and high salinity on sludge filterability.

7.2. Material and methods

7.2.1. Pilot MBRs

Two identical pilot-scale MBRs, each with a total working volume of 85 L, were operated in parallel and fed with sewage. The total hydraulic retention time (HRT) was 10 hrs. Both MBRs were operated at a sludge retention time (SRT) of 50 days. One of the MBRs was used as a reference (no PAC addition) and the other one was dosed daily with 0.8 g of PAC to maintain a 0.5 g L^{-1} PAC concentration in the sludge. More details about the pilot MBRs and the PAC dosage can be found elsewhere (Remy *et al.*, 2009 and Remy *et al.*, 2012).

7.2.2. Sludge fractionation and analyses

Supernatant was obtained from sludge samples with a centrifuge (Sigma, 2-16), operated at 3500 rpm for 15 minutes to remove the solids. After centrifugation, paper filtrate was obtained with a Whatman Black Ribbon filter (589/1, 12-25µm). The soluble fraction was obtained using Cronus PTFE syringe filter with a nominal pore size of 0.45µm. The difference between paper filtrate and the filtrate of the 0.45µm filter will be referred to as the colloidal fraction of the supernatant.

Chemical Oxygen Demand (COD) and total suspended solids (TSS) were determined according to standard methods (APHA-AWWA-WEF, 1998). Concentrations of polysaccharides and proteins were measured according to the methods of Dubois *et al.* (1956) and Bradford (1976), respectively using Glucose and Immunoglobulin G as standards. Free multivalent cations concentrations were measured with an ICP-OES (PekinElmer, Optima 5300DV) in the membrane filtered fraction of the sludge supernatant.

7.2.3. Release of EPS at high salinity

To compare the effect of high monovalent cation concentrations and intensive mixing on the release of EPS on PAC versus non-PAC amended sludge, sludge samples were mixed with a cation exchange resin (CER) is Na^+ form, according to a method proposed by Frølund *et al.* (1996). First, a washing step was performed on the sludge. The sludge was centrifuged at 2000 g (3500 rpm) for 15 min. Sludge pellets were suspended to their original volume in extraction buffer consisting of 2 mM Na_3PO_4, 4 mM NaH_2PO_4, 9 mM NaCl and 1 mM KCl at pH 7. The EPS release test was performed as follows: 300 mL sludge was transferred to a beaker and the cation exchange resin (DOWEX® Marathon® C, Na^+ form, with 70 g g_{VS}^{-1}) was added. The CER has a total exchange capacity of 1.56 mEq g^{-1}, equivalent to an addition of 900 mEq L^{-1} or 52.5 g L^{-1} of salt. The suspension was stirred at 900 rpm to facilitate the release of EPS, and at 4 °C to minimize biological activity. The suspension was sampled after 30 minutes, 1 h, 2 h, 3 h and 4 h. The released EPS were harvested by centrifugation and the fractionation method presented above was applied to determine colloidal and soluble COD, polysaccharides and proteins. The volatile suspended solids (VSS) concentrations were 7.4 and 7.9 g L^{-1}

respectively for the sludges without and with PAC addition. The concentrations of released EPS are presented in mg $gVSS^{-1}$.

7.2.4. Sludge filterability

Sludge from the aerobic tank of the pilot-plant MBRs was recirculated over a five liter filterability set-up with a hydraulic retention time of 1 hour (Figure 1). These vessels contained two flat-sheet membranes, with a surface area of 0.014 m^2 each. The units were equipped with a coarse bubble aerator to scour the membrane surface at a flow rate of 6.6 L min^{-1}. This corresponds to a specific air density of about 28 m^3 m^{-2} h^{-1}. This high value compared to practice was applied to compensate for the broad channel width and the small surface area of the membranes. The trans-membrane pressure (TMP) was monitored on-line (Endress & Hauser, Cerebar M PMC 41).

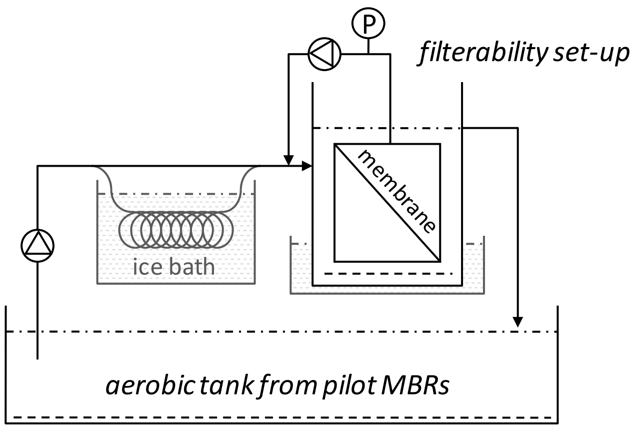

Figure 1 - *Schematic presentation of the filterability set-up.*

Effect of salt - To test the effect of monovalent cations, filtration runs were conducted at a fixed flux of 50 L m^{-2} h^{-1} for 4.5 hours, followed by membrane relaxation during 0.5 hours. The membranes were commercial membranes, made from chlorinated polyethylene with a nominal pore size of 0.4 µm (Kubota). The first filtration was done without additional salt and then repeated, after relaxation, with NaCl addition while stopping recirculation over the pilot plants to avoid dilution of the salt by recirculated sludge. During the second filtration run, after 1h45, 230 mg of Na^+ was added per liter, as NaCl; this corresponds to 10 mEq L^{-1}. This represents about 3 times the Na^+ found in the supernatant of reactors with and without PAC (79.5 mg L^{-1}).

Effect of temperature - The sludge was fed to the filterability set-up where the critical flux was determined at 20, 17 and 14 °C, using the improved flux step method described by Van der Marel *et al.* (2009). The sludge was cooled by circulating it through a cooling spiral submerged in ice to achieve a temperature of 17 °C (Figure 1). To achieve a temperature of 14 °C, the filterability set-up had to be submerged in ice. The filterability set-up was kept at the desired temperature for three hours before starting the critical flux measurements. The temperature was monitored on-line during the test and remained constant. The home-made PVDF membranes with nominal pore size of 0.03 µm were chemically cleaned between each run by soaking in 3000 ppm NaOCl for 2 hours. To exclude errors, caused by differences in membranes, these were exchanged between the filterability tanks after each test, but this had no effect on the critical fluxes that were measured. An empirical relation, introduced by Fan *et al.* (2006), was used to normalize the critical fluxes (JC) to a temperature (T) of 20 °C:

$$JC = JC_{20} \cdot 1.025^{(T-20)} \tag{1}$$

This empirical relation corrects the critical flux for viscosity changes affecting shear-induced diffusion and liquid turbulence, and allows for a comparison of the effect of fouling on the critical flux.

7.3. Results

7.3.1. High salinity

Figure 2 shows that significant amounts of COD were released from sludge flocs to the supernatant over time when sludge and PAC amended sludge were mixed with CER. However, after 4 hours, 16% less soluble COD was released from the sludge with PAC than from the sludge without PAC. For the colloidal fraction, this difference was more pronounced with a 28% lower release for the PAC amended sludge. The colloidal fraction was not only extracted to a lower extent after

4 hours, but also faster with 60% lower release for PAC amended sludge after 30 minutes.

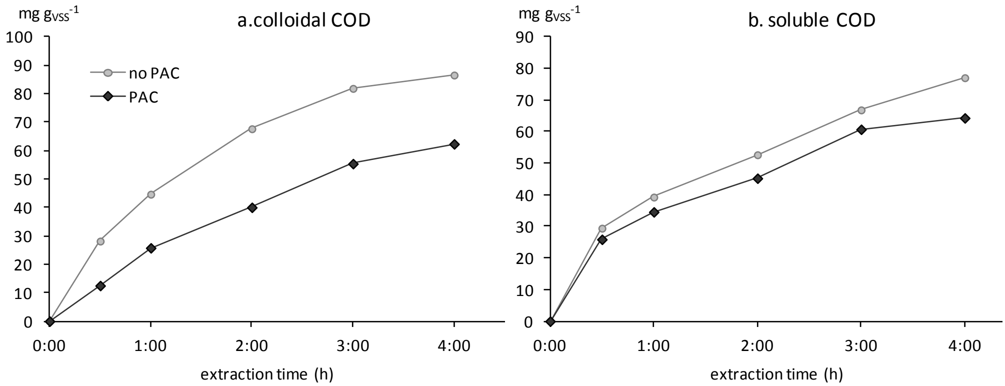

***Figure 2** - COD release from sludge samples mixed with CER in the presence and absence of PAC.*

The amount of extracted EPS with respect to proteins and polysaccharides is presented in Table 1. With both sludges, proteins as well as polysaccharides were released. Whereas the amounts of released proteins were similar, a clear difference was observed for polysaccharides, i.e. after 4 hours respectively 13% and 15% less soluble and colloidal polysaccharides were released from the PAC amended sludge than from the sludge without PAC.

EPS extracted	from sludge without PAC					from sludge with PAC				
extraction time (h)	0.5	1	2	3	4	0.5	1	2	3	4
colloidal (mg g_{VSS}^{-1})										
COD	28.2	44.7	67.7	81.9	86.6	12.5	25.8	40.0	55.4	62.4
proteins	6.1	9.1	12.6	12.6	13.2	3.4	6.7	11.3	11.5	13.2
polysaccharides	3.1	6.3	11.2	13.4	13.3	2.3	2.7	6.2	7.5	11.3
soluble (mg g_{VSS}^{-1})										
COD	29.4	39.3	52.7	66.9	77.1	25.9	34.6	45.3	60.8	64.4
proteins	4.7	6.4	6.9	9.2	9.3	4.8	6.1	6.9	9.0	9.0
polysaccharides	6.1	8.0	9.6	15.5	17.5	3.6	6.7	8.6	14.1	15.2

***Table 1** - COD, protein and polysaccharide release from sludge and PAC amended sludge when mixed with CER.*

Figure 3 compares the course of the TMP during sludge filtration at 50 L m^{-2} h^{-1} in the filterability set-up for sludge without and sludge with PAC. The PAC amended sludge already exhibited a better performance, i.e. a slower TMP increase in time, before salt was added. This is in agreement with previous results (21-23). Immediately after addition of 585 mg L^{-1} of NaCl (232 mg Na^+ L^{-1}) for both sludges, the TMP started to increase at a higher rate, indicating a membrane fouling. However, this increase was less dramatic for the PAC amended sludge. Fouling rates, together with released amounts of Ca^{2+} and Mg^{2+} during the experiments, are presented in Table 2.

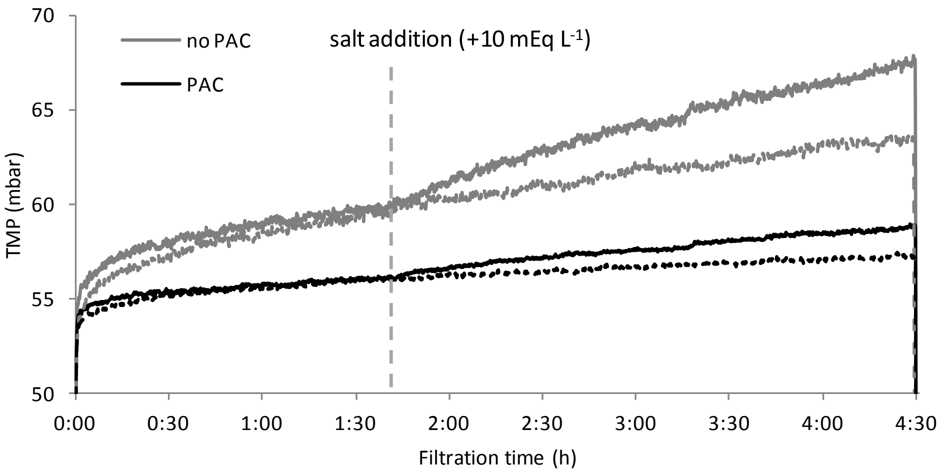

Figure 3 - *TMP response of sludge with and sludge without PAC to NaCl addition (dotted lines represent the TMP during the first run when no salt was added).*

		without PAC	with PAC
fouling rate	without salt	2.16	0.72
(Pa min^{-1})	with salt	4.61	1.59
multivalent cations released	Ca^{2+}	10.1	1.2
(mg L^{-1})	Mg^{2+}	4.7	2.7

Table 2 - *Fouling rates and released divalent cations after salt addition.*

For both sludge types the fouling rates were well below 10 Pa min^{-1}, which was defined by Van der Marel *et al.* (2009) as the boundary condition for critical flux.

Nevertheless, the difference in fouling rate between the two sludges is obvious, with a less detrimental effect of the salt addition on fouling of the PAC amended sludge. A similar effect was also shown for home-made PVDF membranes (results not shown).

This negative effect of salt on the fouling rate was accompanied by a release of Ca^{2+} and Mg^{2+}. Starting values for these divalent cations were 67.1 and 70.6 mg Ca^{2+} L^{-1} for the sludge without PAC and with PAC, respectively and 12.7 and 12.4 mg Mg^{2+} L^{-1} for the sludge without PAC and with PAC, respectively. The effect of NaCl addition on Ca^{2+} and Mg^{2+} release was most pronounced for the sludge without PAC and much stronger for Ca^{2+}. The release of Fe^{3+} and Al^{3+} was also measured as, similarly to Ca^{2+} and Mg^{2+}, they are known to play a role in EPS binding. However, both these cations were below detection limits. Combined for Ca^{2+} and Mg^{2+}, their release respectively represents 10 and 3% of the 10 mEq L^{-1} Na^{+} charge equivalents that were added to the sludge without PAC and the sludge with PAC.

7.3.2. Low temperature

Critical fluxes for sludge without and with PAC were determined at 14, 17 and 20 °C and these fluxes were normalized to 20 °C according to equation (1) to correct for viscosity effects (Figure 4). The average JC_{20} at 20 °C for sludge without PAC of 73.4 L m^{-2} h^{-1} was considerably lower than the average JC_{20} for sludge with PAC of 83.1 L m^{-2} h^{-1}. These values are similar to those found during previous experiments with the same sludge (Remy *et al.*, 2009). Lowering the temperature to 17 °C only reduced the normalized critical flux by 3.0 and 1.8% for sludge without PAC and the sludge with PAC, respectively. However, at 14 °C the difference between the two sludge types becomes apparent with a decrease of the normalized flux of only 2% for the PAC amended sludge compared to 20 °C and a decrease of 24% of the normalized flux at 20 °C for sludge without PAC.

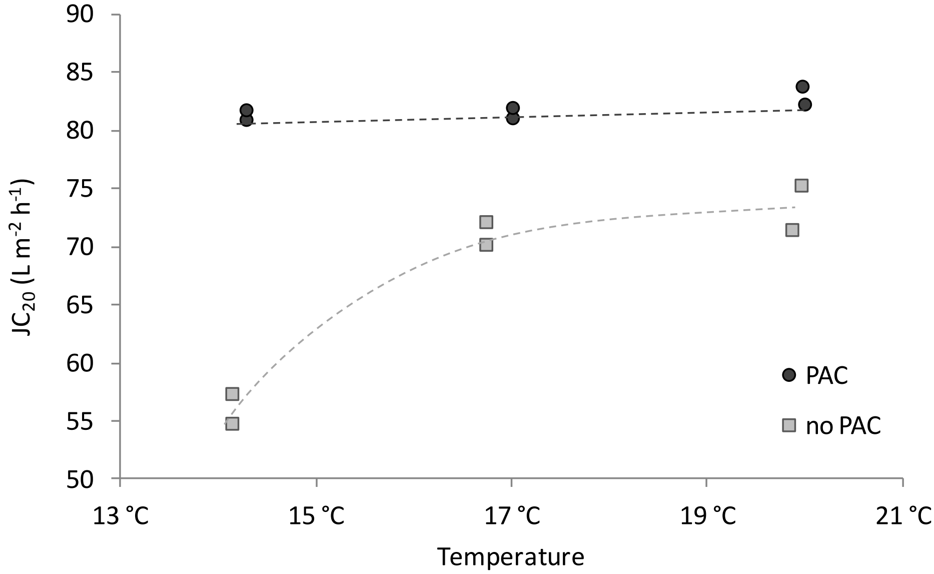

***Figure 4 -** Effect of temperature on the (normalized) critical flux for sludge without and sludge with PAC.*

supernatant concentrations (mg L^{-1})	14 °C no PAC	14 °C PAC	17 °C no PAC	17 °C PAC	20 °C no PAC	20 °C PAC
soluble						
COD	34	31	37	34	37	35
proteins	2.9	2.0	3.2	2.5	3.2	2.5
polysaccharides	4.9	5.2	7.0	6.9	10.4	7.2
colloidal						
COD	11	6	9	2	6	2
proteins	2.5	2.2	4.6	2.9	1.5	0.9
polysaccharides	2.5	0.8	3.4	0.3	2.2	0.8

***Table 3 -** Effect of temperature on supernatant concentrations of COD, proteins and polysaccharides for sludge without and with PAC.*

During the temperature experiments samples were taken from the sludge and these were fractionated to determine colloidal and soluble COD, polysaccharides and proteins (Table 3). Although all the concentrations were rather low and therefore unreliable, in general lower concentrations were found for PAC amended sludge than for sludge without PAC. The effect of the temperature on the concentrations remains unclear. Only for colloidal COD, the concentrations were slightly higher at lower temperatures with a more pronounced effect for the sludge without PAC.

7.4. Discussion

Previous research already had demonstrated that PAC, when applied at low concentrations and long SRTs, helps to reduce membrane fouling and allows for a higher sustainable flux (Remy *et al.*, 2009 and Remy *et al.*, 2012). It was also shown that this positive effect of PAC can be attributed to the formation of stronger sludge flocs with lower shear sensitivity (Remy *et al.*, 2010).

In this study the effect of PAC addition to MBRs was explored to counteract the known negative effects of elevated concentrations of Na^+ and lower temperatures on sludge filterability. Mixing of sludge samples with a cation exchange resin in Na^+ form resulted in a strong release of COD, proteins and polysaccharides. In particular the latter are known membrane foulants (Rosenberger *et al.*, 2006, Lesjean *et al.*, 2004 and Drews *et al.*, 2007) and were released to a lower extent with PAC amended sludge than with sludge without PAC. These experiments however were conducted at very high Na^+ concentrations and strong shearing conditions. In experiments at a much lower Na^+ concentration (230 mg L^{-1}) the filterability of sludge without and sludge with PAC was tested. Immediately after Na^+ addition the filterability of both sludge deteriorated. In the case of PAC amended sludge this effect was considerably lower than for sludge without PAC. PAC amended sludge exhibited a lower release of Ca^{2+} and Mg^{2+} from the sludge floc, confirming the theory by Sobeck and Higgins (2002) that divalent cations are important for the floc integrity and that monovalent cations such as Na^+ have a detrimental effect on floc strength. Although these observations reflect short-term filtration behavior, and do not include long-term adaptation of the sludge to higher monovalent cation concentrations, it shows that PAC addition could have a beneficial effect on membrane performance when treating saline wastewaters in e.g. the textile, petroleum, leather and food industry. Continuous addition of PAC not only could provide a means to obtain a more robust sludge with an average higher filterability, but could also be applied as a control measure in case of salt shocks associated with batch-wise production processes.

Not only a higher viscosity, but also more membrane fouling are causes of a lower sludge filterability at low temperatures. Short-term experiments at three different temperatures of 20, 17 and 14 °C showed that at 14 °C the (normalized) critical flux of sludge without PAC was much lower than the critical flux of PAC amended sludge. In particular for municipal wastewater treatment in MBRs, PAC addition could be a useful strategy in winter time to maintain a higher flux. Similarly to the effect of salt, this was only tested for temperature shocks and a possible adaptation of the sludge to lower temperatures was not considered. Therefore, such a strategy should also be tested for longer periods of a low temperature. A higher colloidal fraction of the supernatant, known to increase the fouling (Rosenberger *et al.*, 2005 and Jarustthirak *et al.*, 2002), was measured at lower temperatures, especially for the sludge without PAC. In contrast to the effect of salt, a clear relation between a low temperature and the presence of higher concentrations of potential membrane foulants such as proteins and polysaccharides could not be confirmed. This relationship however cannot be excluded because during membrane filtration, in close proximity of the membrane surface the sludge flocs are exposed to more shear, and under these circumstances foulants such a proteins and polysaccharides may have released and fouled the membrane. A similar phenomenon was also discussed by Remy *et al.* (2010 and 2012).

7.5. Conclusions

The short-term effect of low dosages of PAC was tested on membrane performance in MBRs at high salinity and low temperatures. Both these conditions cause enhanced membrane fouling, which can be counteracted by addition of low concentrations of PAC. PAC amended sludge showed better resistance to extremely high salinity regarding the release of foulants from the sludge flocs. When submitted to a moderate salinity, the sludge where PAC was dosed showed a lower fouling behavior. The sludge without PAC showed a clear decrease of the critical flux when the temperature was lowered down to 14°C, while the PAC amended sludge sustained a relatively high critical flux.

7.6. Acknowledgements

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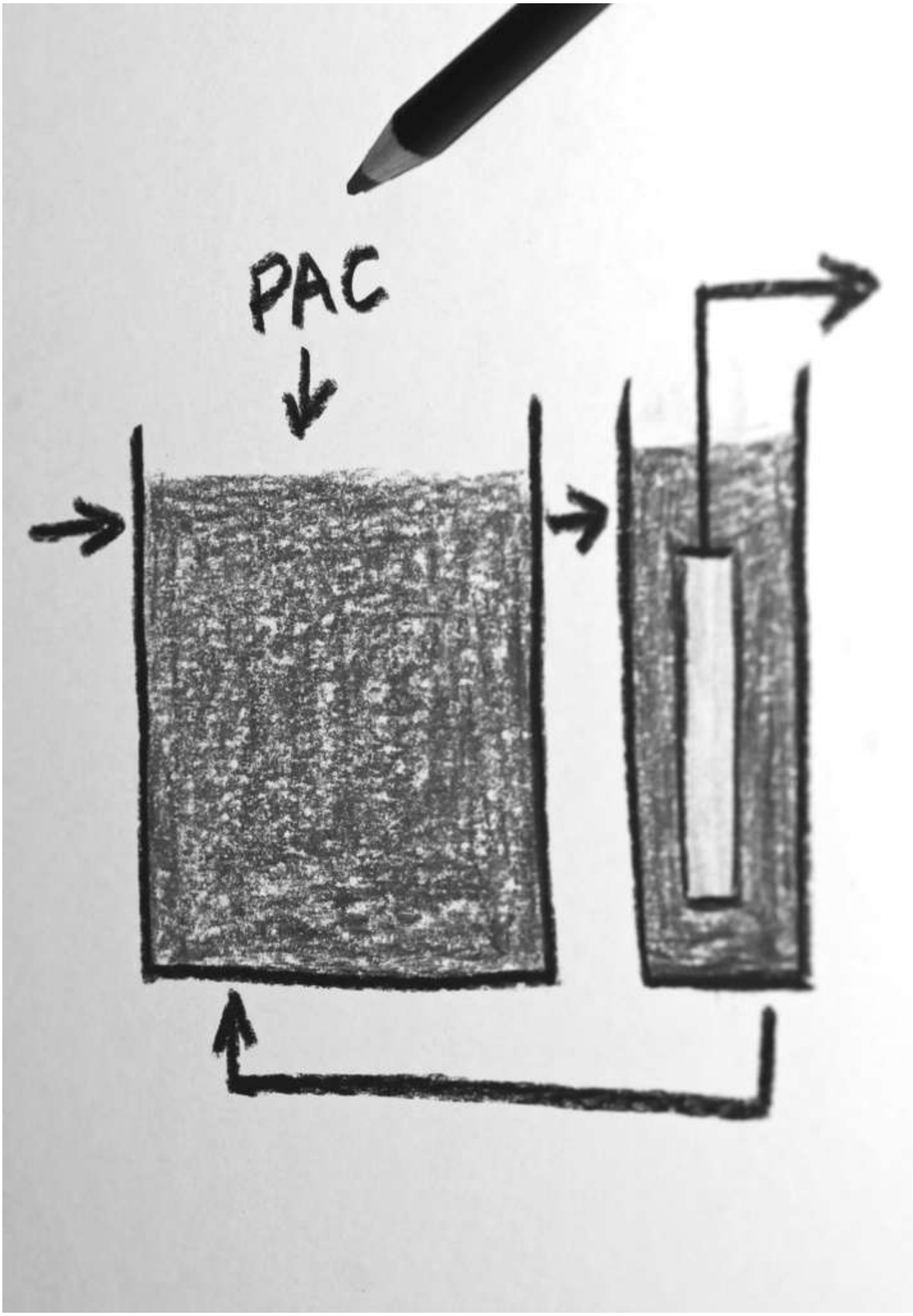
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Chapter 8. CONCLUSIONS, DISCUSSION AND OUTLOOK

8.1. Introduction

Compared to conventional activated sludge systems (CAS), which employ settlers to separate (biological) sludge from treated wastewater, membrane bioreactors (MBRs) offer several advantages, including a smaller footprint and an improved effluent quality. However, the application of MBRs is severely hampered by membrane fouling (Judd, 2011). This results in higher operational costs, because more energy is required to keep the membranes clean and because chemicals and time are required for thorough cleanings once irreversible fouling has occurred. Fouling also results in higher capital costs because a larger membrane area needs to be installed.

Extensive research was already conducted on the effects of membrane properties and membrane operational conditions on fouling (e.g. van der Marel, 2009). In this thesis, the characteristics of the feed to the membranes, i.e. the sludge mixture, were investigated to get a better understanding of their effect on membrane fouling (figure 1) and to identify control measures to manipulate these characteristics such that fouling can be reduced.

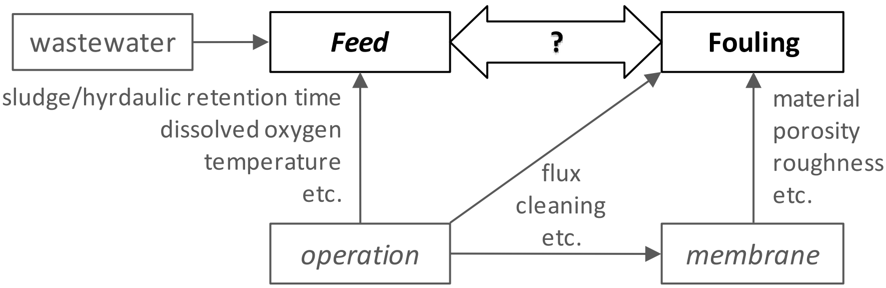

Figure 1 *- Schematic representation of factors affecting fouling.*

8.2. Main findings of this thesis

8.2.1. Flocculation and sludge filterability

As illustrated in figure 1, no clear understanding of the relation between sludge properties and filterability was available. This relation therefore was investigated in more detail with a monitoring study in the full-scale MBR treating municipal wastewater in Varsseveld, The Netherlands, operated by the Water board Rijn & IJssel. Floc fragments, colloidal particles and extracellular polymeric substances (EPS) were found to play an important role in the filterability of the sludge. This was confirmed in laboratory experiments. High shear caused deflocculation and deteriorating sludge filterability. Subsequent reflocculation under conditions of lower shear caused a (partial) recovery of this filterability.

In the proximity of the membrane, a high shear is imposed on the sludge flocs to promote back transport of particles and prevent their deposition as a fouling layer on the membrane surface (Cui *et al.*, 2003). It was therefore hypothesized that the focus should be on making sludge flocs stronger, i.e. less sensitive to shear. This should result in a lower release of foulants when the sludge flocs are in the vicinity of the membrane.

8.2.2. Addition of powdered activated carbon to decrease fouling

One of the options to improve sludge filterability is the addition of powdered activated carbon (PAC). In literature, several mechanisms were proposed to explain a positive effect of PAC on sludge filterability, i.e. a more permeable cake layer if formed on the membrane surface (e.g. Ying & Ping 2006), potential foulants such as exopolymers are adsorbed by the PAC (e.g. Ng *et al.*, 2006), an improved scouring of the membrane surface by the PAC particles (Park *et al.*, 1999) and an improved floc strength (e.g. Li *et al.*, 2005).

In this study a low dosage of PAC, combined with a long sludge retention time (SRT) was selected as the most promising strategy to improve sludge filterability, while keeping the costs as low as possible. While studies presented in literature used concentrations up to eight grams per liter (Ng *et al.*, 2005), a PAC concentration of only half a gram per liter of sludge (corresponding to only 4 mg of PAC per liter of wastewater) and a SRT of 50 days were selected in this study. The PAC only represented approximately five percent of the solids in the reactor. A low concentration of PAC not only was selected to minimize the costs. At higher concentrations, free PAC particles could result in severe scouring of the membranes potentially causing structural membrane damage (e.g. 5 g L^{-1}, Park *et al.*, 1999). Mesoporous PAC was selected to promote microbial growth on the PAC surface and allow microorganisms to access the adsorbed foulants, and in this manner offer the possibility for their biodegradation.

With two bench-scale MBR systems treating municipal wastewater, the filterability of PAC amended sludge was measured and compared to the filterability of sludge without PAC addition. The sludge from the bench-scale reactor with PAC addition exhibited a much better filterability: the critical flux, above which fouling of the membranes becomes severe, was more than 10% higher. When monitoring the bench-scale MBRs for more than a year, less frequent chemical cleanings of the membranes were found to be necessary for the reactor with PAC amended sludge, and a 70% longer sustainable filtration time between two cleanings was possible. Furthermore, the MBR with PAC addition was able to run much longer at fluxes up to 30% higher when compared to the reference sludge. Experiments to determine the mechanisms that caused the improved filterability of PAC amended sludge confirmed the hypothesis of an improved flocculation and enhanced floc strength.

8.2.3. Other advantages of PAC addition on MBR performance

PAC addition not only improved sludge filterability, but also other performance parameters. First of all, a better permeate quality with respect to COD was observed. Even though this improvement was small (5%), it was consistent. PAC amended sludge also resulted in a slightly better removal of a selection of (spiked) organic micropollutants. However, this only was marginal and a higher PAC dosage would be necessary to obtain a substantial micropollutant removal efficiency.

Oxygen transfer also improved (by 10%) when PAC was added to the sludge. This probably was caused by a combination of more compact flocs and a lower viscosity of the PAC amended sludge (Germain & Stephenson, 2005) compared to sludge without PAC. A 45% lower sludge volume index (SVI) was measured for the sludge with PAC addition. Although a lower SVI, i.e. a better sludge settleability is not very relevant for MBR systems, it also indicates a better dewaterability of the sludge (Li & Yang, 2007). This may substantially decrease the costs associated with sludge disposal.

When submitted to conditions of biological stress, i.e. a low temperature and a high salinity, the PAC amended sludge responded much better by a lower degree of deflocculation and less release of potential membrane foulants. This lower sensitivity to temperature and salinity shocks makes MBR operation more robust, not only for municipal wastewater treatment but also for treatment of industrial wastewater where sudden changes in environmental conditions are common. In addition, during periods of low sewage temperatures, typically below 12 °C, sludge foaming, which causes problems in wastewater treatment plants (You & Sue 2009), was frequently detected in the MBR without PAC addition whereas foaming did not occur at all in the MBR with PAC.

8.3. Economical feasibility and energy savings

Based on the results of Van Bentem *et al.* (2010), who reported on 5 years of operational experience with the Varsseveld MBR, an estimation of the cost savings that can be achieved by PAC addition was made. This cost analysis focused on the energy consumption as this still is the main bottleneck for a more widespread application of MBRs (Judd, 2011).

Advantages that are likely to decrease the energy consumption when PAC is dosed are the improved oxygen transfer and the possibility to operate a MBR at higher fluxes. Aeration of the sludge constitutes an important fraction of the energy costs for MBR and conventional activated sludge systems (CAS) (Van Bentem *et al.*, 2010). The combination of CAS and a sand filter (CAS+SF) has an energy consumption of 0.65 kWh m^{-3} while the Varsseveld MBR has an energy consumption of 0.77 kWh m^{-3} (figure 2). CAS+SF was selected as the reference system because the effluent quality of a MBR is closer to the effluent quality of a CAS+SF (Van Bentem *et al.*, 2010).

The possibility to apply higher fluxes will allow a lower installed membrane surface area. This will not only result in lower investment costs, but also in a lower energy demand to provide air for membrane scouring. The amount of air (aeration MT in figure 2) to scour the membranes is proportional to the membrane surface as the specific aeration demand of the membrane (SADm in Nm^3 m^{-2} h^{-1}) is membrane specific. A decrease of membrane aeration and the associated energy demand by 30% is expected, given the potential increase in (average) flux. A 10% improved oxygen transfer would result in 10% lower aeration demand for the sludge tank (aeration AT in figure 2) (Krampe & Krauth, 2003). Obviously these savings still need to be confirmed in a full-scale study.

As shown in figure 2, PAC addition to the MBR would result in a reduction of 13% of the energy consumption of the Varsseveld MBR, i.e. from 0.75 to 0.66 kWh m^{-3}. Although the details for energy consumption of the units of the CAS+SF system are not provided, this implies that the energy consumption of the MBR becomes similar to the energy consumption of a CAS + SF combination. Given an energy price of 0.09 € per kWh (Nuon zakelijk, 2011), PAC addition would save 0.008 € per treated m^3 of water. The costs for 4 mg PAC L^{-1} of wastewater (corresponding to 0.5 g PAC L^{-1} of sludge at a SRT of 50 days) are 0.008 € per m^3 of wastewater, which is comparable to these savings.

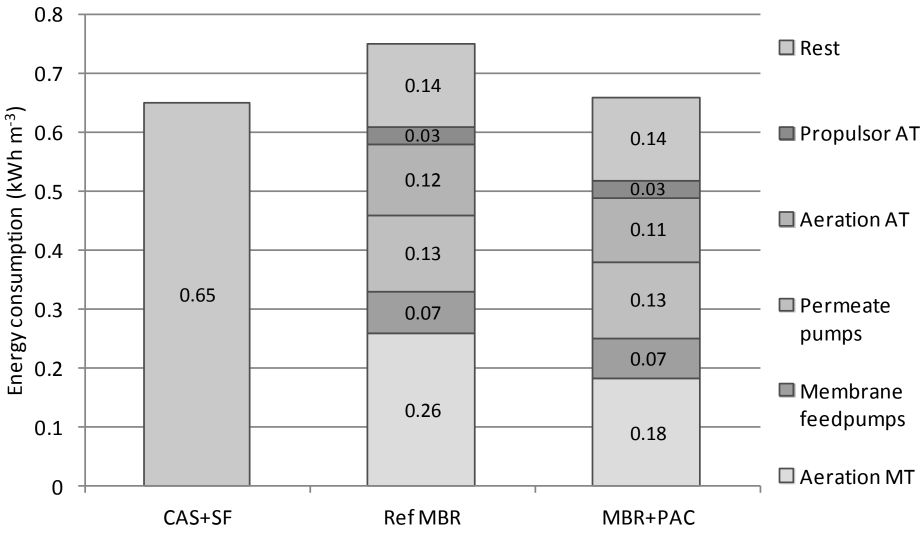

***Figure 2** - Electricity consumption for CAS+SF, reference MBR and MBR+PAC, adapted from Van Bentem et al. (2010).*

When only energy savings are taken into account, PAC dosage therefore hardly seems economically feasible. Nevertheless, this estimation on savings does not take into account the improved effluent quality and lower sensitivity to changes in environmental conditions such as lower temperatures and salinity shocks. PAC would also result in lower costs for cleaning agents and less cleaning time because less frequent chemical cleanings would be possible. A lower investment also would be required because of lower membrane area necessary due to a potential flux increase up to 30%. Finally, a decreased frequency of chemical cleaning probably will lengthen the life time of the membranes (Puspitasari *et al.*, 2010), reducing costs that need to be made for membrane replacement.

The longer SRT and enhanced dewaterability would result in a lower volume of excess sludge, despite the additional 5% solids due to the addition of PAC. Sludge treatment and/or disposal costs are an important fraction of the operational costs and are related to the water content of the excess sludge (STOWA 2010). When sludge can be dewatered to a higher extent, it has a higher energy value and requires lower costs for transport and treatment.

8.4. Main conclusions

In this research, a relation between flocculation and membrane fouling was found. As a solution to improve flocculation and floc strength, the addition of powdered activated carbon was selected and further investigated. The main conclusions of this investigation are:

a. A low dosage of PAC to the sludge, combined with a long SRT is a sustainable and economically viable option to minimize membrane fouling in MBRs.

b. By improving floc strength, PAC decreases the sensitivity of the flocs to shear and stress that otherwise would disrupt the flocs and lead to the release of membrane foulants.

c. Not only does PAC reduce fouling, but it also improves the operation of the MBR with respect to oxygen transfer and sludge dewaterability.

Although the study presented in this thesis was conducted on a long-term basis (approximately one year), and on real municipal wastewater, the fluctuations in the conditions of the reactor were lower than the fluctuations that can be expected in full scale reactors because the research reactor was in the lab where the temperature and flow rate were relatively constant. Full-scale tests should take place to confirm the earlier mentioned advantages of PAC addition.

8.5. Recommendations for further research

8.5.1. Further costs reductions

Even lower PAC concentrations than those applied in this study could still have the same positive effects. While in literature, PAC addition only was investigated at considerably higher concentrations (e.g. Fang *et al.*, 2006), a lower amount than applied in our research was not tested yet. Further decreasing the PAC concentration would result in a proportional decrease in the costs. This option should be tested to find the optimum concentration regarding cost and effects. The PAC type used in this thesis was on the high end of the price scale with two Euros per kilogram (Boere & Van den Dikkenberg, 2006). Other, cheaper PAC types should also be investigated.

Adsorption of membrane foulants did not appear to be the decisive mechanism to obtain the improved filterability of PAC amended sludge. Non activated carbon powder therefore may also be used as a cheaper option. The micro/mesoporous structure of the PAC may not be necessary as it increases the surface area which does not seem to be a sine qua non condition for the improvement of floc strength by PAC addition.

PAC recycled from a post-treatment adsorption step, where components such as humics or micropollutants are adsorbed, could possibly be used instead of virgin PAC as adsorbed compounds did not appear to get released when PAC is incorporated in the sludge flocs. In this manner loaded PAC would be given a second life, enhancing the filterability of the sludge.

Other cheaper alternatives such as bentonite or small sand particles also could be investigated, although too high a density could limit their incorporation within the sludge flocs and the particles would settle in the bottom of the reactor. Long term tests with these alternatives should be conducted to verify whether the same positive effect on the operation of the MBR is possible as with PAC.

8.5.2. Non-continuous dosage

The advantages of PAC addition appeared to be the clearest during stress conditions, such as an increased salinity and lower temperature. PAC addition therefore could be limited to periods of biological stress. For example, PAC addition can only be done during winter conditions when the temperature of the sludge can decrease dramatically and monovalent cations concentration can increase in the MBR because of the salt and brine spread on the roads to counter icing. Furthermore, the startup period of a MBR can also be problematic, before the sludge is fully grown and adapted. PAC addition during startup should also be studied as it has the potential to ease the startup period regarding fouling when the sludge is not yet acclimated to MBR conditions.

Stress periods can lead to the need to over-dimension the membrane surface area as an MBR should be able to handle the entire flow, even under those conditions when a lower flux has to be set. Improving the filterability of the sludge by dosage of PAC during those periods, would allow a design of MBRs with a lower membrane area running constantly at higher fluxes. This would also result in a lower energy consumption.

8.5.3. PAC dosage for other wastewater treatment applications

Low PAC dosages could also be tested in anaerobic MBRs, where fouling also is a major concern. Jeison (2007) found anaerobic sludge to be very sensitive to shear. High shear is required to scour the membrane from foulants but also disrupts the sludge flocs and therefore enhances the release of membrane foulants. Improvement of floc strength by PAC dosage could result in an improvement of the operation of anaerobic MBRs. Hu and Stuckey (2007) already demonstrated that dosing 1.7 g L^{-1} PAC in anaerobic MBR with 4.5 g L^{-1} sludge concentration improves COD removal and reduces fouling. The possibility to reach similar results at a lower PAC dosage should be investigated.

Industrial wastewater treatment plants can face sudden changes in temperature and/or salinity of the influent. To compensate for those fluctuations, large buffer tanks are often used to level off the quantity and quality of the wastewater. By improving the robustness of the treatment plants, PAC addition could allow them to face those variations without the need for massive buffer tanks and allow the application of MBRs on those streams.

PAC addition could also be studied for conventional activated sludge systems (CAS) as an improved oxygen transfer and settleability would also increase the efficiency of such a system. In addition, the improved dewaterability for MBR sludge may also be valid for excess sludge from CAS systems and in this manner PAC could contribute to lower the costs for sludge disposal and/or treatment, which represents an important part (40-60%) of the operating costs of wastewater treatment plants.

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membrane
sludge
PAC
fouling
wastewater
flux
activated
MBR
MBRs
addition
treatment
filterability
low
flocculation
amended
effect
foulants
surface
flocs
lower
high
strength
potential
decrease
concentration
parameters
improvement
properties
municipal
SRT
days
increase
membranes
shown
salinity
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Varsseveld
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retention
large
showed
biological
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presence
structure
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filtration
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becomes
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produced

SUMMARY

Human activity produces a large amount of (polluted) waste water. Before this wastewater is discharged to surface waters, or can be reused, it needs treatment. Usually this is accomplished in conventional activated sludge (CAS) systems. In these systems, the pollutants in the wastewater are degraded by microorganisms (biological sludge) that must be subsequently separated from the treated water in large sedimentation tanks. To improve the effluent quality of the wastewater treatment plant (WWTP), or to allow easier post-treatment if reuse of this effluent is anticipated, the clarifiers can be replaced by membranes. The resulting system is referred to as a membrane bioreactor (MBR). An additional advantage of an MBR is that it requires a much smaller footprint compared to a CAS system.

Unfortunately, membrane fouling is inherent in the filtration of sludge containing waters resulting in lower flux through the membranes and/or increased energy demand. The effects of membrane properties and operational parameters on fouling in MBRs have been intensively studied, but little was known prior to this work about the impact of feed properties, i.e. sludge mixture composition, on membrane fouling. Thus, the aim of this study was to investigate which parameters of the sludge are responsible for fouling in MBRs, and to find a solution for membrane fouling by influencing these sludge properties.

In **Chapter 2**, the startup of the first full-scale Dutch MBR in Varsseveld is reported with special attention to the properties of the sludge mixture. The studied parameters are then correlated to membrane fouling. The constituents in sludge supernatant, i.e. the fraction of the sludge mixture once the sludge flocs are removed, and more specifically the concentration of particles larger than 0.45 µm (the colloidal fraction), give the strongest contribution to membrane fouling. It is also shown that this fraction does not originate from the wastewater but is produced during the biological treatment process itself. Additionally, filterability improves as the sludge becomes more hydrophobic which is in turn a reflection of the strength of the flocs. The filterability of the sludge of the MBR in Varsseveld improved considerably after wastewater containing cheese-covering-polymer was uncoupled from the wastewater flow and iron chloride addition started in order to remove additional phosphate. Multivalent cations such as ferric ions have been

reported to improve the flocculation of activated sludge. From these results, flocculation was hypothesized to play a major role in the filterability of the sludge as schematized in figure 1.

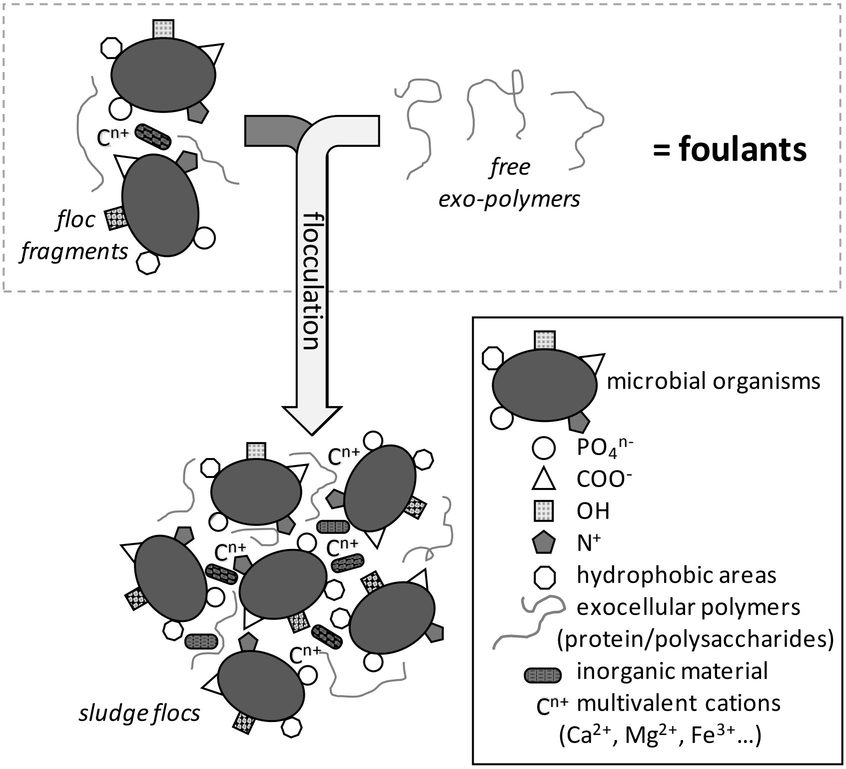


***Figure 1** - Schematic representation of an activated sludge floc and potential membrane foulants.*

Chapter 3 confirms the relation between fouling and flocculation hypothesized in chapter 2 through batch tests where activated sludge disruption by shear results in a higher fouling of the membranes while reflocculation leads to a lower fouling by the sludge. After compiling the parameters responsible for improving the floc strength, the addition of powdered activated carbon (PAC) was selected to decrease fouling. The hypothesized role of PAC addition is that it gets incorporated in the flocs and improves their structure (figure 2). PAC was selected because it has the potential to provide other advantages as well such as additional removal of potentially dangerous organic compounds such as pharmaceuticals and trace compounds of personal care products. These compounds are present in municipal wastewater but are hardly biodegraded in WWTPs. To keep the costs low yet retain efficacy, a combination of low PAC dose and a long solids retention time was selected.

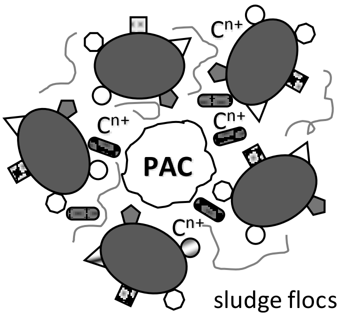


Figure 2 - *Improved floc structure in the presence of PAC.*

The effect of PAC was investigated in two pilot-scale MBRs treating municipal wastewater. **Chapter 4** shows the effect of PAC addition on sludge filterability. Using a filterability setup where the sludge was recirculated it was shown that the combination of a low PAC dosage (0.5 g L^{-1} of sludge) with a relatively long sludge retention time (SRT) of 50 days resulted in an improvement of approximately 10 percent of the critical flux. The critical flux is the flux above which the trans-membrane pressure (TMP) increase becomes too high for sustainable operation; it is an indicator of the maximum flux at which an MBR can be operated. A strong increase of the filtration period without significant fouling at high fluxes of 50-72 L m^{-2} h^{-1} and a decrease of gel deposition on the membrane surface after a long filtration period were also observed. Furthermore, gels which deposited on the membrane surface at high fluxes could be removed with less effort. Finally, a slightly better effluent quality could be produced in the PAC amended MBR.

In **Chapter 5**, several mechanisms which could explain the positive effect of a low PAC dosage on sludge filterability are investigated in a series of batch experiments. An enhanced membrane scouring or adsorption of membrane foulants on the PAC surface could not explain this positive effect. Instead, the formation of stronger sludge flocs in the presence of PAC was found to be the most likely explanation. This is attributed to a higher shear resistance and a lower release of foulants in the vicinity of the membrane where the shear is highest to accomplish back-transport of potential foulants away from the membrane surface.

In **Chapter 6,** the effect of PAC addition on the treatment and operation performances of MBRs is investigated over a period of 320 days in two pilot-scale MBRs treating municipal wastewater running in parallel on the same influent. It is shown that the combination of a low PAC dosage (0.5 g L^{-1} of sludge) with a relatively long SRT of 50 days results in a 70% improvement of the sustainable filtration time. The sustainable flux, i.e. the operational MBR flux which did not produce unacceptable fouling, could be increased by 30%. A consistent, albeit slight, improvement of the permeate quality was also observed. Furthermore, other advantages from PAC addition were observed including an improved oxygen transfer by 11%, and a probable increase of the dewaterability as indicated by a 45% lower sludge volume index, which is a measure of the settleability of the sludge.

In **Chapter 7**, the short-term effect of low dosages of PAC on membrane performance in MBRs operated at high salinity and low temperatures is discussed. Both these conditions cause enhanced membrane fouling, which can be counteracted by addition of low concentrations of PAC. PAC amended sludge showed better resistance to extremely high salinity as a lower concentration of foulants was released from the sludge flocs when the sludge was submitted to those conditions. When exposed to a moderate salinity, the PAC amended sludge exhibited a lower fouling behavior. The sludge without PAC dosing showed a clear decrease of the critical flux when the temperature was decreased down to 14°C, while the PAC amended sludge sustained a relatively high critical flux.

In **Chapter 8**, the main conclusions drawn from the different chapters are summarized and discussed. The potential savings in energy and installation costs for a PAC amended MBR are evaluated, and PAC addition is found to be economically feasible. Possible strategies to further decrease the costs by using an alternative to PAC or reducing the concentration in the sludge, as well as non-continuous dosing are discussed. Potential applications for other treatment plant configurations such as conventional activated sludge systems, industrial wastewater treatment and anaerobic MBRs are also presented. It is recommended that full-scale investigations are conducted in order to verify whether similar effects can be found in practice.

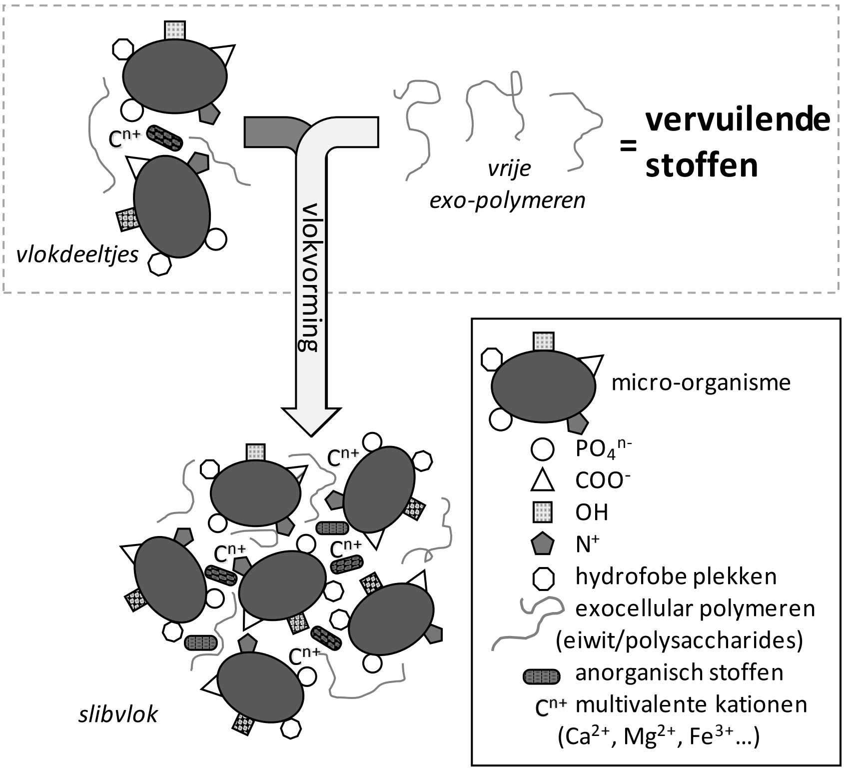

slib
PAK
MBR
stoffen
membraanvervuiling
afvalwater
vervuiling
filtreerbaarheid
flux
effect
membraan
lage
lagere
toevoeging
vlokvorming
vlokken
vervuilende
condities
systemen
actief
dosering
verbetering
parameters
hoge
lange
eigenschappen
gewijzigde
zoals
kritische
kwaliteit
filtratie
zoutgehalte
Varsseveld
dagen
verminderen
onderzocht
besproken
membraanoppervlak
potentiële
concentratie
combinatie
waargenomen
aangetoond
resulteert
periode
behandeling
slibvlokken
duurzame
verbeterd
effluent
relatief
verblijftijd
voordelen
uitgevoerd
vervolgens
operationele
zeggen
geproduceerd
prestaties
pilootschaal
geselecteerd
energie
structuur
werden
gemeld
verbeteren
full-scale
aanwezigheid
gevonden
kosten
water
waarbij
afgebroken
conventionele
verschillende
effecten
Bovendien
behandelden
verwijderd
extra
waar
membranen
verklaren
hogere
bekend
positieve
waarschijnlijke
stedelijk
leidt
onderzoeken
twee
biologisch
mengsel
stijging
fractie
hoog
verantwoordelijk
verbeterde
verondersteld
grote
rol
terwijl

SAMENVATTING

Door menselijke activiteiten wordt een grote hoeveelheid (vervuild) afvalwater geproduceerd. Voordat dit afvalwater op het oppervlaktewater kan worden geloosd, of in aanmerking komt voor hergebruik, dient het gezuiverd te worden. Meestal wordt dit gedaan in zogenaamde conventionele actiefslib (CAS) systemen. De verontreinigende stoffen worden afgebroken door vlokvormende micro-organismen en deze vlokken worden vervolgens in grote bezinktanks van het gezuiverde water afgescheiden. Om de kwaliteit van het gezuiverde water verder te verbeteren of geschikter te maken voor nabehandeling met het oog op hergebruik, kan overwogen worden om de bezinktanks te vervangen door membranen. In dat geval ontstaat een zogenaamde membraanbioreactor (MBR). Een bijkomend voordeel van MBR systemen is dat ze een veel kleiner grondoppervlak nodig hebben dan CAS systemen omdat grote bezinktanks niet langer nodig zijn, en omdat hogere concentraties micro-organismen vastgehouden kunnen worden waardoor ook de biologische reactor kleiner kan worden uitgevoerd.

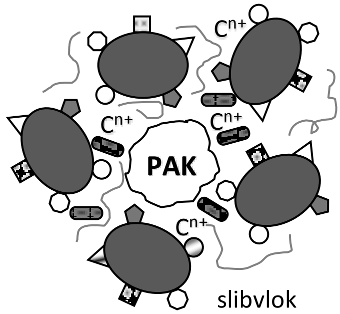
Echter, het optreden van membraanvervuiling kan nooit voorkomen worden en het gevolg is een lagere flux door de membranen en/of een verhoogd energieverbruik om de membranen schoon te houden. Terwijl de effecten van membraaneigenschappen en membraanoperationele parameters op de vervuiling in MBR systemen reeds intensief zijn bestudeerd, is slechts weinig studie gedaan naar de invloed van de eigenschappen van het te filtreren mengsel, in dit geval het mengsel van (gezuiverd) afvalwater en slibvlokken (het actiefslib). Het doel van deze studie was dan ook om te onderzoeken welke slibeigenschappen verantwoordelijk zijn voor de membraanvervuiling in MBR systemen, en om een methode te vinden om deze eigenschappen dusdanig te manipuleren dat de membraanvervuiling drastisch kan worden gereduceerd.

In **Hoofdstuk 2** werd de opstart van de eerste full-scale Nederlandse MBR voor de behandeling van huishoudelijk afvalwater in Varsseveld gevolgd, waarbij de relatie tussen de eigenschappen van het te filtreren actiefslibmengsel en de (membraan) filtreerbaarheid van dat mengsel centraal stond. Hieruit bleek dat de bestanddelen in het supernatant van het slib (na centrifugeren), en meer specifiek de concentratie van deeltjes groter dan 0.45 micrometer (de colloïdale fractie) in dat supernatant, de sterkste bijdrage aan de membraanvervuiling gaven. Tevens werd aangetoond dat deze deeltjes niet afkomstig waren van het te behandelen afvalwater maar tijdens de biologische behandeling werden geproduceerd. Ook werd een positieve correlatie aangetoond tussen de hydrofobiciteit en sterkte van de slibvlokken enerzijds en de filtreerbaarheid van het slib anderzijds. De filtreerbaarheid van het slib verbeterde aanzienlijk nadat afvalwater van een kaasmakerij, met daarin een polymeer dat als kaasdekmiddel werd gebruikt, werd losgekoppeld van de afvalwaterstroom. Ook het doseren van ijzerchloride om extra fosfaat uit het afvalwater te kunnen verwijderen had een positief effect op de filtreerbaarheid. Uit deze resultaten werd geconcludeerd dat de vorming en degradatie van de slibvlokken een centrale rol speelt bij de filtreerbaarheid van actiefslib (figuur 1).



***Figuur 1 -** Schematische weergave van een actief slib vlokken en potentiële membraan vervuilende stoffen.*

In **Hoofdstuk 3** werd de relatie tussen membraanvervuiling en vlokvorming, zoals in hoofdstuk 2 werd vastgesteld, bevestigd met behulp van een aantal batchtesten. In deze testen werd actiefslib blootgesteld aan sterk verhoogde afschuifkrachten. Hoewel dit resulteerde in een aanzienlijke stijging van de membraanvervuiling, lieten de testen ook zien dat, zodra de verhoogde afschuifkrachten werden weggenomen, re-flocculatie optrad, en de membraanvervuiling sterk afnam. Uit een aantal methoden die de gemiddelde vloksterkte zouden kunnen verbeteren, werd de toevoeging van actieve kool in poedervorm (PAK) geselecteerd om membraanvervuiling te verminderen. De veronderstelde rol van de PAK was dat het wordt opgenomen in de vlokken en hun structuur verbetert (figuur 2). Bovendien heeft PAK het potentiële voordeel dat het potentieel gevaarlijke maar niet biologisch afbreekbare organische stoffen kan verwijderen die in lage concentraties in het afvalwater aanwezig zijn, zoals geneesmiddelen en persoonlijke verzorgingsproducten. Om de bijbehorende kosten te beperken, werd gekozen voor een combinatie van een lage dosis PAK en een lange verblijftijd van het slib in het zuiveringssysteem.



Figuur 2 - *Verbeterde vlokstructuur in de aanwezigheid van PAK.*

In **Hoofdstuk 4** werd het effect van PAK op membraanvervuiling onderzocht in twee pilot-scale MBR systemen die werden gevoed met huishoudelijk afvalwater. Met behulp van een opstelling waarmee continue de filtreerbaarheid van het slib kon worden gemeten, werd aangetoond dat door de combinatie van een lage dosering PAK (0.5 g L^{-1} slibmengsel) en een relatief lange slibverblijftijd van 50 dagen de zogenaamde kritische flux met ongeveer 10% kon worden verbeterd. De kritische flux is de flux waarboven de transmembraan druk te hoog wordt voor een langdurige goede werking van de membranen. Ook werd waargenomen dat door de PAK de lengte van periode waarin gefiltreerd kon worden bij relatief hoge fluxen van 50 tot 72 L m^{-2} h^{-1}, en zonder dat noemenswaardige vervuiling optrad, veel langer werd. Verder werd geconstateerd dat aanzienlijk minder gelvorming optrad op het oppervlak van de membranen en dat deze gel veel eenvoudiger kon worden verwijderd dan in afwezigheid van PAK. Tenslotte werd een lichte verbetering van de effluentkwaliteit geconstateerd als gevolg van de PAK dosering.

In **hoofdstuk 5** werden verschillende mechanismen die het positieve effect van een lage dosering PAK op de filtreerbaarheid van het slib zouden kunnen verklaren onderzocht in een reeks batchtesten. Een verhoogde afschuring van het membraanoppervlak door PAK deeltjes of adsorptie van potentiële membraanvervuilende stoffen door de PAK konden dit positieve effect niet verklaren. De vorming van slibvlokken in de aanwezigheid van PAK die beter bestand zijn tegen de verhoogde afschuifkrachten in de nabijheid van het membraan gaf de meest waarschijnlijke verklaring.

In **hoofdstuk 6** werd het effect van PAK op de behandeling en de prestaties van twee MBR systemen onderzocht gedurende een periode van 320 dagen. Beide MBR systemen behandelden huishoudelijk afvalwater en aan de een werd PAK gedoseerd en aan de ander niet. De combinatie van een lage PAK dosering (0.5 g L^{-1} van slib) en een relatief lange slibverblijftijd van 50 dagen resulteerde in een 70% langere “duurzame” filtratietijd. De duurzame flux, dat wil zeggen de operationele flux die geen onacceptabele vervuiling geeft, kon met 30% worden verhoogd. Tevens werd een kleine maar consistente verbetering van de permeaatkwaliteit waargenomen. Opvallend was dat ook de zuurstofoverdracht met 11% verbeterde en de slibvolume index, een maat voor de bezinkbaarheid van het slib, 45% lager was. Dit laatste duidt erop dat de ontwaterbaarheid van het slib door de aanwezigheid van PAK aanzienlijk was toegenomen hetgeen grote voordelen kan hebben voor de verdere behandeling van dat slib.

In **hoofdstuk 7**, werd het korte termijn effect van PAK op de membraanprestaties bij hoge zoutgehaltes en lage temperaturen bestudeerd. Beide situaties worden in de praktijk aangetroffen en kunnen de membraanvervuiling drastisch doen toenemen. Slib met PAK bleek veel beter bestand te zijn tegen extreem hoog zoutgehaltes en er kwamen veel minder membraanvervuilende stoffen vrij uit het slib. Ook indien het werd blootgesteld aan een matig zoutgehalte vertoonde het slib met PAK minder membraanvervuiling dan slib zonder PAK. Het slib zonder PAK gaf een duidelijke afname van de kritische flux indien de temperatuur werd verlaagd (van 20 tot 14°C), terwijl in het geval van het slib met PAK een relatief hoge kritische flux gehandhaafd kon worden.

In **hoofdstuk 8** werden de belangrijkste observaties van deze studie samengevat en bediscussieerd. De potentiële besparingen in energie en installatiekosten voor een MBR met PAK dosering werden geëvalueerd, en hieruit bleek dat PAK dosering economisch haalbaar is. Mogelijke strategieën om de kosten nog verder te verlagen door het gebruik van een alternatief voor PAK, door het verlagen van de concentratie PAK in het slib, of door het discontinue doseren van PAK, werden besproken. Ook werden potentiële toepassingen van PAK dosering voor andere zuiveringsinstallaties zoals CAS systemen, industriële afvalwaterzuiveringsinstallaties en anaërobe MBR systemen gepresenteerd. Wel werd aanbevolen om op praktijkschaal onderzoek te doen of vergelijkbare effecten kunnen gevonden worden.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RESUME

L'activité humaine produit une grande quantité d'eaux usées (polluées). Avant que ces eaux usées ne puissent être déversées dans les eaux de surface, ou éventuellement réutilisées, un traitement est nécessaire. Habituellement, cela se fait à l'aide d'un système à boues activées conventionnelles. Dans ces systèmes, les polluants présents dans les eaux usées sont dégradés par les microorganismes (boues biologiques) qui doivent être ensuite séparés de l'eau traitée dans les larges bassins de sédimentation. Afin d'améliorer la qualité de l'effluent des stations d'épurations, ou pour faciliter le post-traitement si la réutilisation de cet effluent est prévue, les clarificateurs peuvent être remplacés par des membranes. Le système résultant est alors appelé bioréacteur à membrane (BRM). Un avantage additionnel d'un BRM est qu'il nécessite une surface beaucoup plus petite par rapport à un système à boues activées conventionnelles.

Malheureusement, le colmatage des membranes est inhérent à la filtration des boues, entraînant une baisse du flux à travers les membranes et/ou une demande d'énergie accrue. Les effets des propriétés des membranes et des paramètres opérationnels sur le colmatage dans les BRM ont été intensivement étudiés. Cependant, avant cette étude, peu était connu sur l'impact des propriétés du liquide à filtrer, comme la composition du mélange de boues, sur le colmatage des membranes. Ainsi, l'objectif de cette étude est d'étudier les paramètres des boues responsables du colmatage des membranes dans les BRM, et de trouver une solution à ce colmatage en influençant ces propriétés des boues.

Dans le **chapitre 2**, le démarrage du premier BRM municipal néerlandais, à Varsseveld, est rapporté avec une attention particulière portée aux propriétés du mélange de boues. Les paramètres étudiés sont ensuite corrélés au colmatage des membranes. Les constituants présents dans le surnageant des boues, c'est à dire la fraction du mélange une fois que les flocs de boues sont enlevées par décantation, et plus précisément la concentration de particules de plus de 0,45 µm (la fraction colloïdale), donnent la plus forte contribution au colmatage des membranes. Il est également montré que ces composés colmatants ne proviennent pas uniquement des eaux usées, mais sont également produits pendant le processus de traitement biologique lui-même. De plus, avec

l'amélioration de la filtrabilité, les boues deviennent plus hydrophobes, ce qui est à son tour le reflet de la solidité des flocs. La filtrabilité de la boue du BRM de Varsseveld a été considérablement améliorée après que les eaux usées industrielles contenant du polymère utilisé pour recouvrir les fromages aient été découplées du débit des eaux usées et que du chlorure de fer ait été dosé dans le BRM en vue d'éliminer le phosphate supplémentaire. Les cations multivalents, tels que les ions ferriques, ont été signalés comme améliorant la floculation des boues activées. De ces résultats, l'hypothèse selon laquelle la floculation joue un rôle majeur dans la filtrabilité des boues, comme schématisé dans la figure 1, a été émise.

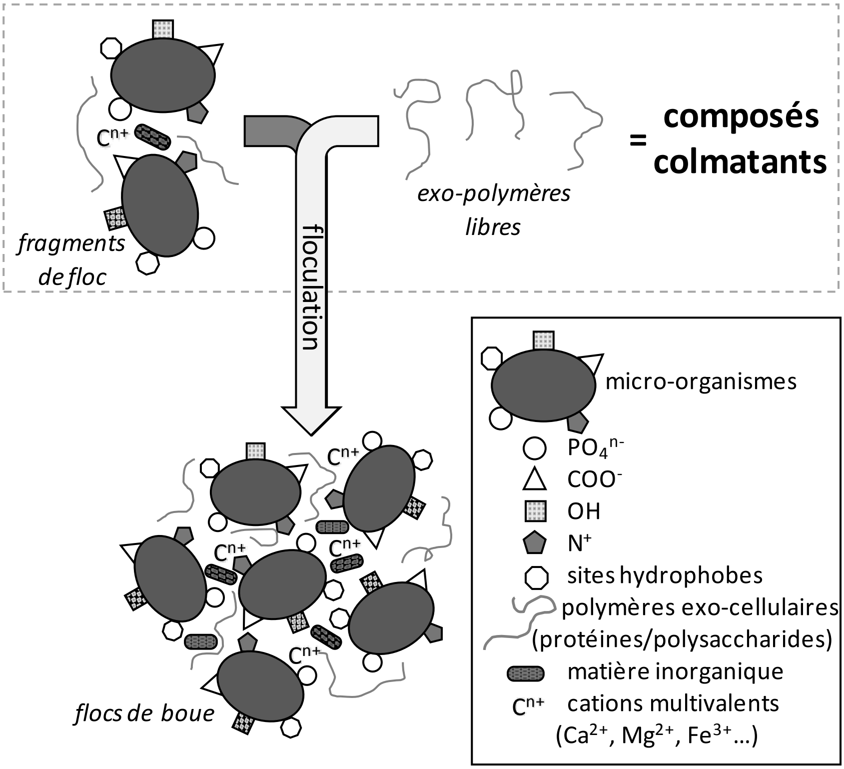

***Figure 1 -** Représentation schématique d'un floc de boues activées et colmatage potentiel de la membrane.*

Le **Chapitre 3** confirme la relation entre le colmatage des membranes et la floculation présupposée dans le chapitre 2, par des tests par lots où la perturbation des flocs de boue activée résulte en un plus important colmatage des membranes tandis que la reflocculation conduit à une baisse de ce colmatage par les boues. Après avoir compilé les paramètres responsables de l'amélioration de la solidité des flocs, l'ajout de charbon actif en poudre (CAP) a été choisi afin de minimiser le colmatage des membranes. Le rôle supposé de l'addition de CAP est qu'il est incorporé dans les flocs et améliore leur structure (figure 2). Le CAP a été choisi parce qu'il a le potentiel d'apporter d'autres avantages ainsi que l'élimination additionnelle de composés organiques potentiellement dangereux tels que les produits pharmaceutiques et les traces de produits cosmétiques. Ces composés sont présents dans les eaux usées municipales, mais ne sont que peu biodégradés dans les stations d'épuration. Pour maintenir les coûts bas tout en conservant l'efficacité, une combinaison de faibles doses de CAP et d'un long temps de rétention des solides a été sélectionnée.

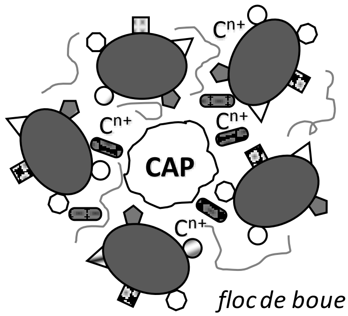

***Figure 2 -** Amélioration de la structure des flocs en présence de CAP.*

L'effet du CAP a été étudié dans deux BRM pilotes opérés parallèlement, traitant des eaux usées municipales. Le **chapitre 4** montre l'effet de l'addition de CAP sur la filtrabilité des boues. En utilisant une configuration dans laquelle les boues étaient recirculées, leur filtrabilité a été mesurée. Il a ainsi été démontré que la combinaison d'une faible dose de CAP (0,5 g L^{-1} de boues) avec un temps de rétention des boues relativement long (50 jours) a entraîné une amélioration d'environ dix pour-cent du flux critique. Le flux critique est le flux au-dessus duquel l'augmentation de la pression transmembranaire devient trop élevée pour une exploitation durable, il est un indicateur du flux maximum auquel un BRM peut être exploité. Une forte augmentation de la période de filtration sans colmatage significatif à flux élevé de 50 à 72 L m^{-2} h^{-1} et une diminution des dépôts

de gel sur la surface de la membrane durant une période de filtration ont également été observées. Par ailleurs, les gels qui ont été déposés à flux élevés sur la surface de la membrane pouvaient être retirés avec moins d'effort. Enfin, une qualité légèrement meilleure des effluents du BRM avec CAP a été constatée.

Au **chapitre 5**, plusieurs mécanismes susceptibles d'expliquer l'effet positif d'une faible dose de CAP sur la filtrabilité des boues sont étudiés dans une série d'expériences par lots. Un décrassement amélioré de la membrane ou l'adsorption des composés colmatants à la surface du CAP ne pouvait pas expliquer cet effet positif. Au lieu de cela, la formation de flocs de boues plus forts en présence de CAP a été jugée comme l'explication la plus probable. Ceci est attribué à une plus grande résistance au cisaillement et une plus faible libération des composés colmatants dans le voisinage de la membrane où le cisaillement est le plus élevé pour accomplir un retro-transport des composés potentiellement colmatant loin de la surface de la membrane.

Au **chapitre 6**, l'effet de l'addition de CAP sur les performances de traitement et de fonctionnement du BRM est étudié sur une période de 320 jours dans les deux BRM pilotes traitant en parallèle les mêmes eaux usées municipales. Il a été montré que la combinaison d'une faible dose de CAP (0,5 g L^{-1} de boues) avec une relativement longue rétention des boues (50 jours) résulte en une amélioration de 70% du temps de filtration durable. Le flux durable, c'est à dire le flux opérationnel du BRM qui ne produit pas de colmatage inacceptable, pouvait être augmenté de 30%. Une constante, quoique légère, amélioration de la qualité des eaux traitées a été également observée. Par ailleurs, d'autres avantages de l'ajout de CAP ont été observés, y compris un transfert d'oxygène amélioré de 11%, et une augmentation probable de la déshydratation des boues comme indiqué par un indice de volume des boues, qui est une mesure de la décantabilité des boues, de 45% inférieur.

Au **chapitre 7**, les effets à court terme de faibles doses de CAP sur la performance des membranes de BRM opérant sous haute salinité et dans des conditions de basses températures sont discutés. Ces deux conditions causent une aggravation du colmatage des membranes, ce qui peut être contrecarré par l'ajout de faibles concentrations de CAP. Les boues modifiées par l'ajout de CAP ont montré une meilleure résistance à la salinité très élevée, comme une concentration plus faible de composés colmatants a été libérée des flocs de boues lorsque la boue a été soumis à ces conditions. Lorsqu'elles sont exposées à une salinité modérée, les boues avec CAP présentaient un comportement moins colmatant. Les boues, sans dosage de CAP, ont montré une nette diminution du flux critique lorsque la température a été diminuée à 14 °C, tandis que les boues avec addition de CAP ont maintenu un flux critique relativement élevé.

Au **chapitre 8**, les principales conclusions tirées des différents chapitres sont résumées et discutées. Les économies potentielles en coûts d'énergie et d'installation pour un BRM avec ajout de CAP sont évaluées, l'addition de CAP est jugée comme économiquement faisable. Les stratégies possibles afin de diminuer encore les coûts en utilisant une alternative au CAP ou la réduction de la concentration dans les boues, ainsi que le dosage discontinu sont discutés. Les applications potentielles pour d'autres configurations de station de traitement des eaux, tels que le système à boues activées conventionnelles, le traitement des eaux usées industrielles et le BRM anaérobie, sont également présentés. Il est recommandé que des études à grande échelle soient menées afin de vérifier si les effets similaires à ceux constatés à l'échelle pilote peuvent être confirmés en pratique.

ACKNOWLEDGEMENT

I could not have finished the redaction of this book alone! This section gives me a welcome opportunity to thank the people who have been helping me during the completion of my thesis.

First of all, I would like to thank my supervisors. Hardy, we started to work together on "fooling" in membrane bioreactors back in 2004 during my MSc thesis with the sub-department of Environmental Technology of Wageningen University, in Bennekom. This research actually came to a negative conclusion as adding ozone to the MBR worsens fouling. Nevertheless, you told me about Wetsus, a research center that was just starting in Leeuwarden, in the heart of Friesland. After looking for "Leeuwarden" on a map, I was interested and decided to join the adventure. Wim then became my promotor for Wageningen University and we started a project together, aiming at decreasing fouling in MBRs by influencing the biology. You both have been extremely helpful in order to complete the research on that subject, write the articles and ultimately this book. Thank you for your input and your patience.

I also have to thank Wetsus as a whole. When I started my PhD, it was still under construction in the remote city of Leeuwarden. All the walls were still plaster; white and clean, until my reactor came along, of course… For what Wetsus has become now, I want to acknowledge the hard work and vision of Johannes, Cees and Gert-Jan as well as the rest of the staff. You have made Wetsus a success and seeing it grow like it did from the inside was a very enriching experience.

Wetsus did not only provide great facilities for completing a thesis, but also a great staff and great colleagues with whom it was always nice to spend time at work, but also outside of work. Of course, I particularly want to thank the PhDs, members and participants in the membrane bioreactor team of Wetsus, for all the interesting discussions during the meetings, the trips and in the office. A special acknowledgement also goes to the students I had the chance to supervise over the years: Lu Lei, Artur, Julien, Léo and Virginie. They could help me keeping my reactor relatively clean and contribute to this research.

I would like to thank all the colleagues from Wetsus, alumni or still busy there. Unfortunately, Wetsus has now grown too big to be able name everybody individually without starting a new book. The time spent at Wetsus has been a great experience in my life. There was a pleasant atmosphere that I really enjoyed. In the lab, in the proefhal, in the office, during the coffee breaks or the "borrels" and even around a few pints in the Irish Pub on Thursday evenings, there was always room for "constructive" discussions about work and miscellaneous subjects.

I also want to acknowledge everybody at the sub-department of environmental technology of the University of Wageningen for their help and always being there to help when that was necessary. Especially during the first months of my thesis and while following the startup of the MBR of Varsseveld, I had the opportunity to work with great and very helpful colleagues, at the now closed facility of Bennekom.

After my contract at Wetsus was finished, I still had quite a bit of writing to do in order to get this book finished. I nevertheless started to work for Sustec, a great and young company in Wageningen. The year I spent there allowed me to learn a lot, not only about thermal hydrolysis, but also about working in a company. For that, I am thankful.

Afterwards, I came back to Friesland, working for Paques, in Balk. Paques is a company where the many different and remarkable offered technologies make working very interesting. I am now working in a great team with the technology department and would like to acknowledge all my colleagues.

Now comes a paragraph in French in order to thank my family and other French people who are infamous for their understanding of English. Ce chapitre de mon livre est là pour me donner l'opportunité de remercier celles et ceux qui m'ont aidé et ont permis l'achèvement de ma thèse. Je vais saisir cette occasion pour remercier mes parents qui m'ont supporté et toujours encouragé à réaliser ce que je voulais. Je tiens à remercier également mon frère et mes (belle) sœurs, Clémence, Bastien, Émeline (tu es finalement devenue Dr avant moi) et Adeline pour leur support. Cette thèse est dédiée à Papy qui a toujours été une source d'inspiration pour moi mais qui ne peut malheureusement pas être là pour en voir la fin car il est parti trop tôt. Une pensée émue va également à Bon Papa lui aussi parti avant la réalisation de ce doctorat. Un grand merci va également à mes grand-mères et à toute la famille. Enfin, une pensée va à ceux qui ont partagé les bancs à l'ISA et pendant le lycée. Mon émigration au pays des tulipes fait que l'on ne se voit pas aussi souvent que je l'aimerais mais c'est toujours un plaisir de se revoir pour partager un verre et les nouvelles.

I also want to acknowledge my paranymphs, Ingo and Régis. You accepted to help me during this exercise and for that I am thankful. Your assistance is much appreciated and I also enjoyed sharing beers and discussions with you on multiple occasions. I am looking forward for your help during the defense.

Last but not least, Cláudia, muito obrigado for the support (even though I never stressed) and pushing me to finish this thesis. A little bit more and you would have been graduating before me…

Maxime Remy

April 2012

ABOUT THE AUTHOR

Maxime Remy was born on the 26th of May 1980 in Lille, France. After High School, he started an engineer education in agriculture, food sciences and environment at the "Institut Supérieur d'Agriculture" in Lille. He went to Wageningen University while taking part in an Erasmus exchange program in September 2002 to spend his fifth and final year of education with the group of environmental sciences. Subsequently, he stayed for one more year in the Netherlands in order to obtain a Master of Science in environmental technology from Wageningen University. He completed his Master thesis within the sub-department of environmental technology in Bennekom. The subject of his thesis was to study the effect of ozone on membrane fouling in membrane bioreactors. From June 2004 till February 2009, he was employed by Wageningen University to work at Wetsus, in Leeuwarden, on the PhD project that led to the redaction of this thesis. After working for one year in Wageningen, at Sustec BV on the development of thermal hydrolysis, he is now working, since November 2010, as a technologist at Paques BV, in Balk, The Netherlands.

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Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment

C E R T I F I C A T E

The Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment (SENSE),
declares that

Maxime José Jean Remy

born on 26 May 1980 in Lille, France

has successfully fulfilled all requirements of the
Educational Programme of SENSE.

Wageningen, 25 May 2012

the Chairman of the SENSE board	the SENSE Director of Education
Prof. dr. Rik Leemans	Dr. Ad van Dommelen

The SENSE Research School has been accredited by the Royal Netherlands Academy of Arts and Sciences (KNAW)

KONINKLIJKE NEDERLANDSE
AKADEMIE VAN WETENSCHAPPEN

The SENSE Research School declares that **Mr. Maxime José Jean Remy** has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 49 ECTS, including the following activities:

SENSE PhD courses

- Environmental Research in Context
- Research Context Activity: Co - redaction of a proposal for a European project within the 7th Framework program: "Sustainable and Innovative Solutions for Treatment and Management of Sludge" (SISTEMS)
- Basic and Advanced Statistics

Other PhD and MSc courses

- Basics in Membrane Technology
- Labview Basics
- Debating course
- Techniques for Writing and Presenting Scientific Papers
- Project Management and Time Planning
- Teaching and supervising thesis students
- PhD competence assessment

Oral Presentations

- Interaction between biological design and operation and fouling in MBRs, Network Young Membrains 7th Edition, 22 – 24 June 2005, Enschede, The Netherlands
- Link between flocculation and fouling in an MBR, Sensible water technology SENSE Symposium, 12 – 13 April 2007, Leeuwarden, The Netherlands
- Decrease fouling in MBRs by adding powdered activaded carbon, Novel cost effective technologies for wastewater treatment and bio-energy production SENSE Symposium, 4 - 5 September 2008, Wageningen, The Nederlands
- Decrease fouling in MBRs by influencing biology, Network Young Membrains 10th Edition, 18 – 19 September 2008, Berlin, Germany
- Effect of low dosages of powdered activated carbon on MBR performance, 29 October – 4 November 2011, Amsterdam, The Netherlands

SENSE Coordinator PhD Education and Research

Mr. Johan Feenstra