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INFLUENCE OF INORGANIC AND ORGANIC MATTER IN GRAVITY DRIVEN MEMBRANE ULTRAFILTRATION

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Men love to wonder, and that is the seed of science.

Ralph Waldo Emerson

To Everyone who is part of my life. All of You simply make it wonderful.

Ania Chomiak, April 2015

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FREQUENTLY USED ABBREVIATIONS

AOC	Assimilable Organic Carbon
ATP	Adenosine Triphosphate
CWF	Clean Water Flux
Dex	Dextrans
DOC	Dissolved Organic Carbon
EPS	Exopolymeric / Extracellular Polymeric Substances
FEG	Field Emission Gun
GDM	Gravity Driven Membrane
GPC	Gel Permeation Chromatography
HMW	High Molecular Weight
HOR	Horizontal
HRT	Hydraulic Retention Time
kDa	kilo Dalton
LC-OCD	Liquid Chromatography-Organic Carbon Detection
LMW	Low Molecular Weight
MW	Molecular Weight
OCT	Optical Coherence Tomography
PBBR	Packed Bed Bioreactor
PBS	Phosphate Buffered Saline
POU	Point Of Use
PSS	Polystyrene sulfonate
SD	Standard Deviation
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SSF	Slow Sand Filter
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
TS	Total Solids
UF	Ultrafiltration
VCD	Variable Contrast Detector
VER	Vertical
VS	Volatile Solids

ZUSAMMENFASUNG

Die Membranfiltration ist attraktiv für die Trinkwasseraufbereitung, da sie Partikel sicher zurückhalten kann. Nachteile der Membranfiltration sind die hohen Kosten, verursacht durch den Energie- und Chemikalienverbrauch, sowie das sogenannte Fouling, welches die Effizienz der Filtration stark beeinträchtigen kann. Eine wichtige Form des Foulings ist das Biofouling bzw. Biofilmwachstum. Biofilme können die Permeabilität der Membran stark beeinträchtigen und werden in der Regel durch regelmässige, chemische Reinigung entfernt (Flemming 2002).

Die schwerkraftgetriebene Ultrafiltration (gravity driven membrane (GDM) filtration) ist ein neues Betriebskonzept (Derlon et al. 2014, Peter-Varbanets et al. 2010), bei dem das Biofilmwachstum auf der Membranoberfläche zugelassen wird. Der Filtrationsprozess wird einzig durch die Schwerkraft angetrieben (ohne Stromverbrauch) und funktioniert bei sehr tiefem Transmembrandruck (wenige mbar). Die Akkumulation von organischen Stoffen und Partikeln auf der Membranoberfläche während der dead-end Filtration wird zugelassen. Das Vorhandensein eines aktiven Biofilms ermöglicht dabei einen stabilen Langzeitbetrieb des Filtersystems ohne Reinigung.

Das Ziel dieser Arbeit war es, die Wechselwirkung zwischen der Biofilmbildung und der Akkumulation von organischen Schmutzstoffen und anorganischen Partikeln zu verstehen. Die Schmutzstoffe und Partikel beeinflussen in schwerkraftgetriebenen Membransystemen massgeblich die Quantität und Qualität des produzierten Filtrats. Die konkrete Fragestellung lautete: (i) wie beeinflussen organische und anorganische Modellpartikel das Wachstum und die Struktur des Biofilms und den dadurch entstanden hydraulischen Widerstand? (ii) wie kann der Biofilm durch Hydrolyse und Abbau der Schmutzstoffe die Permeatqualität bei schwerkraftbetriebenen Membranen verbessern?

Die Resultate zeigen, dass der Biofilm zwar den grössten Beitrag am Filtrationswiderstand hat, dass aber die Akkumulation von kleinen (im µm-Bereich), homogenen, anorganischen Partikeln den Widerstand weiter erhöhen und den Permeatflux verringern kann. Grössere, heterogene, anorganische Partikel hingegen können diesen Negativeinfluss reduzieren und die Permeabilität erhöhen. Auf die organischen Schmutzstoffe kann der Biofilm folgende Auswirkungen haben:

- Die Schmutzstoffe werden vollständig abgebaut, wenn die Fracht konstant und die Kontaktzeit der Schmutzstoffe mit dem Biofilm genügend gross ist.

- Die Schmutzstoffe werden zu kleineren Fraktionen hydrolisiert und nur unvollständig abgebaut, wenn die Fracht und die Kontaktzeit variieren. Dies führt zu einer Verschlechterung der Permeatqualität, weil die kleinen Fraktionen von der Membran nicht vollständig zurückgehalten werden können.

- Organisches Substrat wird vom Biofilm in Abhängigkeit von dessen Alter und Aktivität aufgenommen oder abgegeben. Eine biologische Vorbehandlung des Zuflusses in Kombination mit GDM Filtration kann helfen die Qualität des Ablaufs zu verbessern.

Die Resultate dieser Arbeit stützen das Bestreben, dass die Kombination von Biofilm und Membran in naher Zukunft ein relevantes Filtrationssystem werden soll als Alternative zu klassischen Membransystemen. Das Zusammenspiel von Biofilm, Membran und Schmutzstoffen muss weiter untersucht werden, weil bei Ultrafiltration mit tiefem Druck die Schmutzstoffe eine Biofilmbildung stark beeinflussen. Hierbei sollen nicht nur Trinkwassersysteme, sondern auch die Aufbereitung von Grauwasser und allenfalls auch Anwendungen im Abwasserbereich betrachtet werden.

SUMMARY

The main advantage of membrane filtration processes is efficiency of separation, which allows to reach very high quality treated water. However, main disadvantages are cost of the treatment (electricity, chemicals) and membrane fouling, which can severely reduce the efficiency of the filtration process. Biofouling and biofilm formation is a major type of fouling due to biological deposition and activity on any membrane type surface. Biofilms on membranes significantly reduce permeation rates, and as such are removed and controlled by using chemical treatments (Flemming 2002).

Gravity driven membrane (GDM) ultrafiltration is a new concept (Derlon et al. 2014, Peter-Varbanets et al. 2010) to treat water that allows natural biofilms to develop on the membrane surface. The water is filtered with use of gravity force (no electricity) at very low transmembrane pressure (mbar). All organic and biological matter are allowed to accumulate on the membrane surface during filtration (dead-end type). The biofilm development and its activity on the membrane allows for stable, long term operation of the filtration system without cleaning requirements.

The aim of this work was to identify interactions between biofilm development and model inorganic and organic foulants accumulation onto permeate quantity and quality produced in GDM system. The specific questions were: (i) how inorganic particles and model organic foulants can influence biofilm accumulation and structure, and in turn physical resistance to filtration, (ii) how biofilm presence can improve permeate quality produced during the GDM filtration due to hydrolysis and degradation of the foulants.

Results indicate that while biofilm itself has the highest resistance to filtration, small (micron size) and homogenous inorganic particles accumulation can add to this resistance and further reduce permeate fluxes. Presence of larger, heterogeneous inorganic particles can counterbalance the negative results of small particle accumulation and increase the permeation.

For the organic foulants, biofilms can:

- degrade the foulant fully, if the load of the foulant is constant and biofilm-foulant contact time sufficient. This leads to permeate quality improvement.
- hydrolyse the foulant to smaller size fractions, followed by incomplete degradation, if the load of the foulant and thus biofilm-foulant contact time is variable. This leads to permeate quality decline due to permeation of the small fractions through the membrane.
- uptake or release the assimilable organic carbon (AOC) depending on the age and activity of the biofilm. Biological feedwater pre-treatment can help to favour removal of AOC in the system.

From outcome of this work it is further proposed that "biofilm-membrane" composite becomes a relevant filtration system in the near future, as opposed to traditional "membrane-only" systems. The biofilm-membrane-foulant interactions need to be investigated further, since the foulants strongly influence biofilm development in the low pressure ultrafiltration. This should be conducted not only for drinking water systems, but also for grey water reuse and possibly wastewater.

Chapter 1

General Introduction

Introduction

In this thesis influence of inorganic and organic matter on biofilm development and permeate quantity and quality in gravity driven membrane (GDM) ultrafiltration is investigated. The focus is on how the inorganic particles influence biofilm structure, and in turn the permeate quantity. The second focus is how organic matter influences biofilm accumulation and growth, and at the same time how the biofilm activity influences the permeate quality due to the organic matter degradation. Balance between production of assimilable organic carbon (AOC) due to hydrolysis of accumulated biomass and removal of the AOC by the biofilm to produce biologically stable permeate water is also investigated.

The introduction into the thesis focuses on (i) types of membrane processes and their applications (ii) membrane fouling types with focus on biofouling (iii) negative and positive roles of biofilms in membrane filtration and ultimately (iv) interactions between biofilm and organic and inorganic matter in gravity driven membrane ultrafiltration.

Membrane systems

The first documented membrane filtration experiment was conducted by Schmidt in 1856 and involved separation of soluble Acacia with use of bovine heart membranes (Schmidt 1856). The first use of the term "ultrafilter" and the first synthetic membranes preparation was done by Bechhold in 1907 (Bechhold 1907). However, the golden age of membrane science and development period was in the 1960s and 1980s, when first defect free, high flux cellulose acetate membranes have been fabricated (Loeb and Sourirajan 1963) and applied practically. Today membrane separation processes are efficient and well established for treating different types of waters: from lightly contaminated surface waters to heavily contaminated industrial, as well as municipal wastewaters. The main advantages of membrane filtration are high process stability, combined with efficiency of separation, which allows to reach high quality treated water. The disadvantages are cost of treatment due to high electricity (to push the feedwater across the membrane surface) and periodic chemical treatments, as well as the investment costs.

The membrane separation characteristics depend mainly on membrane material (chemistry) and pore size. For porous membranes the pore size determines the primary retention capacities of the membrane, with smaller pores retaining smaller

contaminants. In non-porous membranes the molecules transported across the membrane need to be first dissolved in the polymeric membrane matrix in order to be transferred by diffusion mechanism (Vrentas and Vrentas 2002) The retention capability non-porous membranes is high and reaches the level of dissolved ions (Fig. 1).

But the more efficient membrane separation comes with a price – the smaller the pore size, the more energy is needed to push the feedwater across the membrane. Four main membrane categories for water treatment exist, and their typical removal capabilities are presented in Fig. 1.

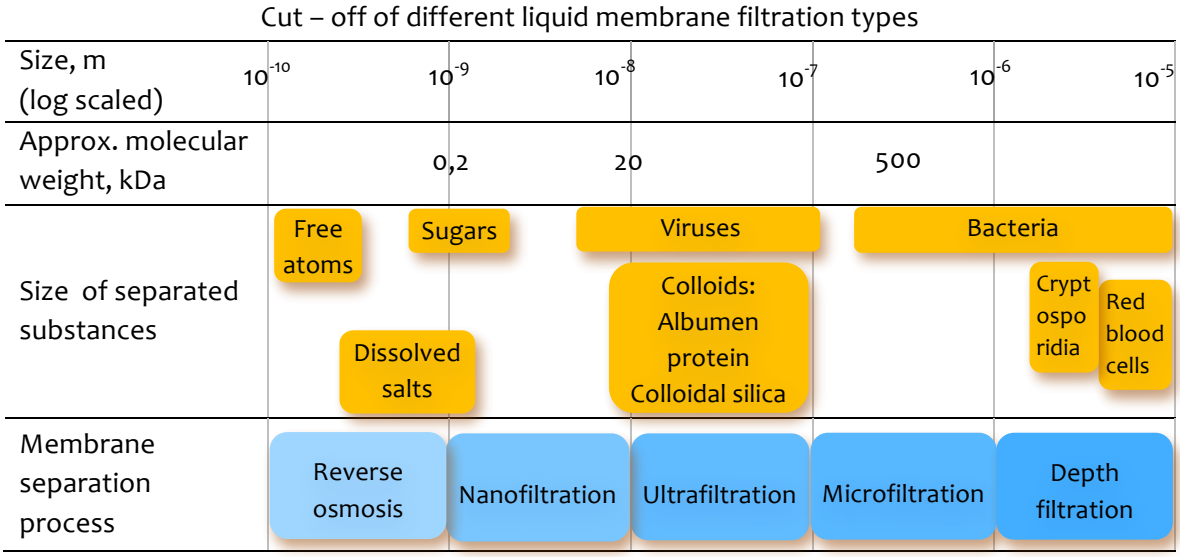

Figure 1 *Overview of membrane pore sizes, removed contaminants and the applications (AWWA 2005).*

Membrane fouling

For clean membranes with larger pore sizes (in micro and ultrafiltration) transport is primarily convective and depends on level of pressure applied on the feed stream. Water flux is therefore directly proportional to the applied pressure (Eq. 1):

$$J = {}^{TMP}/_{\eta R_{total}} \qquad [L\,m^{-2}\,h^{-1}] \qquad (1)$$

where J is a volume of water V [L] flowing through a defined membrane area A [m^2] per time t [h], TMP is a transmembrane pressure [Pa], R_{total} is total resistance to filtration [m^{-1}] and η is dynamic water viscosity [Pa∗s].

During filtration, accumulation of inorganic and organic matter occurs at the membrane surface, which leads to increase of the resistance to water passage R and thus flux decline.

The total resistance to filtration R_{total} can be estimated during the filtration and expressed by Eq. 2:

$$R_{total} = R_{membrane} + R_{cake} + R_{biofilm} + R_{osm.} + R_{gel} + R_{irrev.} \qquad [m^{-1}] \qquad (2)$$

where $R_{membrane}$ is the clean membrane resistance, R_{cake} is resistance due to particle (solids) deposition on the membrane surface, $R_{biofilm}$ is resistance due to biological growth on membrane and R_{irrev} is the resistance due to irreversible fouling (i.e., sorption). $R_{osm.}$ is resistance due to osmotic pressure exerted by the solutes (macromolecules such as proteins) accumulated at the membrane wall, while R_{gel} resistance comes from gel formed with the macromolecules (Nakao et al. 1979). Both R_{osm} and R_{gel} refer to accumulation of macromolecules at the membrane wall, but to this date there is no clear agreement on under what filtration conditions (trans-membrane pressure, bulk macromolecules concentration) the osmotic or gel formation limitations dominate. Both gel and osmotic pressure terms are often used interchangeably (Denisov 1994), also R_{gel} is often referred to as R_{cake} (Wang and Rodgers 2008). However, as demonstrated by Wijmans et al. (1984), the predictions of flux for the gel model can be practically equivalent to the osmotic pressure model for ultrafiltration of macromolecules. Additionally, chemistry of the macromolecules (size, charge, polarity) as well as of the feedwater (pH, ionic strength) is very important in membrane fouling (Cho et al. 2000, Vilker et al. 1981). In practice each type of fouling can be roughly estimated following Eq. (2) by measuring deionised water flow through the examined membrane, after each cleaning sequence. The most common cleaning sequences to remove partial resistance to filtration may include: membrane backflushing ($R_{cake,}$ R_{osm}), chemical cleaning (R_{irrev}), biocidal treatment + backflushing ($R_{biofilm,}$ R_{irrev}).

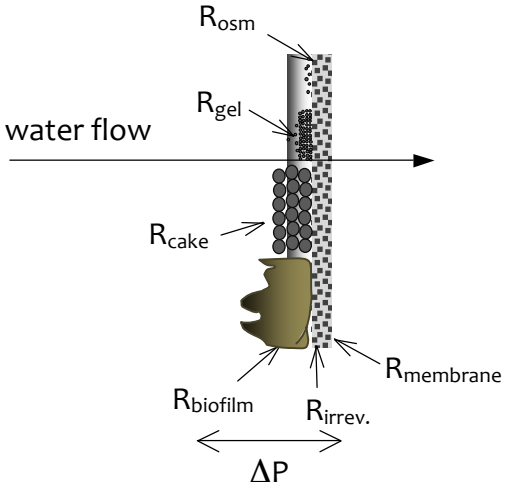

Figure 2 *Partial resistances during membrane filtration that lead to transmembrane pressure loss ΔP.*

There are three main types of membrane fouling, all increase the resistance to filtration R_{total}:

- physical,
- chemical,
- biological.

Because of fouling, conventional membrane systems are either operated in crossflow mode (with shear), or with periodic backwashing when in dead-end mode. GDM ultrafiltration is however operated without shear or backwashing for long periods of time (months).

In the *physical fouling*, the particles and contaminants physically deposit at the membrane surface, or enter the pores of the membrane. The particles accumulation at the membrane surface is called "cake", while deposition of contaminants in the pores is called "pore plugging". In both cases, the overall resistance to water flow is increased, and thus permeate flux decreased (assuming constant transmembrane pressure filtration). Cake and pore plugging are mainly associated with micro- and ultrafiltration due to relatively large pores of the membranes. Traditional cleaning methods include periodic membrane backwashing to remove the accumulated cake mass and release the particles from the pores.

Chemical fouling includes: precipitation of salts (mainly in nanofiltration and reverse osmosis), gelation of macromolecular polymers (ultrafiltration), chemical adsorption to the membrane material (any type of membrane), or reduction of flux due to osmotic pressure imposed by the macromolecules (proteins, humic substances, etc.). Type and extent of chemical fouling depend strongly on feedwater composition, membrane type as well as operational conditions (dead end or crossflow filtration). Due to variety of chemical interactions, typically an autopsy of the chemical fouling type is needed in order to select appropriate cleaning agent and treatment.

Biofouling has been described as "combination of biofilm formation and bacterial adhesion and deposition on the membrane surface" (Le-Clech et al. 2006), "unwanted deposition and growth of biofilms" (Flemming 2002) and as "a biofilm reactor in the wrong place" (Flemming et al. 1997). It is the most problematic type of membrane fouling because microorganisms are ubiquitous in any technical system. All other fouling components such as organic and inorganic dissolved substances and particles can be removed by pretreatment, i.e. flocculation, prefiltration. The microorganisms can however multiply (Flemming et al. 1997).

Therefore removal of even 99.99% bacteria will leave enough cells to grow at the cost of biodegradable foulants present in the water. Thus biofouling and biofilm formation can negatively affect performance of any membrane system, usually considerably reducing permeation rates (Flemming et al. 1997). This is not only due to physical bacteria deposition, but more likely due to the exopolymeric substances excretion by the bacterial activity (Dreszer et al. 2013). The EPS matrix has multiple functions, but primarily it helps bacteria to form the sessile community (biofilm), forms a protective barrier around the bacteria and helps to retain water (Laspidou and Rittmann 2002). Unfortunately, the EPS forms a highly hydrated gel matrix (Nielsen and Jahn 1999) and can be responsible for creating a significant barrier to permeate flow in membrane processes (Le-Clech et al. 2006). In addition, EPS can also posses different viscoelastic properties, behaving more rigid or more fluid (Sweity et al. 2011). When EPS matrix is more fluid, it could penetrate into the membrane pores.

Typical membrane treatments affected by biofouling require constant or periodic biocide treatments (to kill the bacteria), followed by chemical cleaning (to remove the EPS layer from the membrane) (Flemming 2002). Other, more sustainable treatment can include pre-treatment of the feedwater (can be treatment via biological pathway i.e. sand filtration, or chemical way - sorption) to lower or remove the organic foulants concentration, and thus growth potential of the biofilm (Huang et al. 2009, Peldszus et al. 2012).

Positive aspects of biofilm formation

Recent studies report that presence of biofilms on membrane surfaces is not always detrimental. On the contrary, the biofilms can contribute to improving the quality of produced permeate (Derlon et al. 2014, Lu et al. 2013, Shang et al. 2005). For instance, biofilms developed on microfiltration membranes (membrane bioreactors) significantly contributed to increased viruses retention, despite very large pores in relation to virus size (Lu et al. 2013, Shang et al. 2005). In another study Shen et al. (2014) showed increased retention of antibiotics in membrane bioreactor, due to physical biofilm presence. Kang et al. (2007) showed that presence of biofilms on membrane bioreactor surface resulted in removal of small molecular weight organic carbon (< 1 kDa) due to degradation, and increased physical retention of higher molecular weight compounds (> 30 kDa). In the drinking water sector, Derlon et al. (2014) and Peter-Varbanets et al. (2011) showed biopolymer organic carbon retention with the biofilm present on the ultrafiltration membrane surface, during long term river water filtration. Another positive aspect

of biofilm formation is the flux stabilisation phenomena (Peter-Varbanets et al. 2010). Due to biofilm presence on the membrane surface the membrane does not foul completely and the permeate flux never reaches zero. Instead, due to degradation capability of the biofilm and presence of predators (Derlon et al. 2013), it stabilizes at values which can be practically used for drinking water production, currently at decentralised scale (Boulestreau et al. 2012).

With the prices of the membrane materials decreasing and becoming more affordable, a new approach of membrane filtration is emerging. The "biofilm-membrane" filtration concept is more sustainable as opposed to "membrane only" filtration - tolerating biofilm presence on membrane yields lower permeation rates, but allows for stable operation of the system with much less energy and chemical requirements.

Interactions between inorganic and organic matter and biofilm in gravity driven ultrafiltration

Gravity driven membrane ultrafiltration is a specific case of ultrafiltration. Compared to conventional ultrafiltration it is operated in ultralow pressure conditions (mbar) and in continuous dead-end (no shear) filtration mode. Also unlike typical ultrafiltration membrane systems (AWWA 2005) it is operated long term (months) without membrane backwashing or cleaning. It allows for biofilm development on the membrane surface, thus resistances to filtration in GDM can be different from the typical resistance models for dead-end ultrafiltration (Fig. 3). In Fig. 3 the following conceptual models are presented: cake filtration (a), osmotic pressure and gel filtration (b), and compared to biofilm development in the GDM system (c).

In cake filtration model (a), it is assumed that retention of particulate matter leads to proportional increase of the resistance to filtration (assuming the particles are rigid and not compressible (Teoh et al. 2006)). The type of particles (size, shape) determines the porosity and density of the cake, which determines the cake resistance. The continuous particle accumulation ultimately leads to progressive increase of resistance and loss of flux. The resistance increase can be higher when the cakes are composed of similar size particles (Kim and Ng 2007), are compressible (Mendret et al. 2009) or when additional particle-particle electrostatic interactions take place (Faibish et al. 1998).

The cake model assumes continuous cake growth and thus flux loss. It not clear how the accumulating inorganic particles would interact with the biofilm growing on the membrane surface, i.e. influencing the biofilm structure.

Model (b) assumes accumulation of macromolecules (i.e., proteins) at the membrane surface and distinguishes between formation of osmotic or gel layer at the membrane surface. In the initial stages of accumulation the macromolecules impose osmotic pressure resistance to the permeating water, R_{osm}. The concentrated macromolecules possess different rheology than inorganic particles from model (a), displaying characteristics of a solid due to increased viscosity, as discussed in Blatt et al. (1970). With progressing time of the filtration, the increasing concentration of the macromolecules (or shear applied during the filtration, Meireles et al. (1991)) can lead to macromolecules aggregation termed as "gelation" (Maruyama et al. 2001), which leads to R_{gel} resistance. However, in reality it has been shown that it is difficult for the true gel to form, and it would be expected that the true gel has a sharp phase boundary, zero diffusion coefficient and no fluidity (Nakao et al. 1986). Accumulation of macromolecules of medium molecular weight between 10 – 100 kDa would lead more to osmotic pressure resistance, rather than true gel resistance, however this could be more likely under high macromolecules membrane wall concentrations and for higher transmembrane pressures (Wijmans et al. 1984). On the other hand, it was proposed that critical filtered volume determines the mass of accumulated macromolecules and thus determines transition between osmotic and gel limitations (Bessiere et al. 2005). It has been shown that practically these two models can be equivalent to each other with respect to flux prediction (Wijmans et al. 1984). Thus in dead end unstirred ultrafiltration the permeate flux would depend mainly on diffusivity (without shear) of the macromolecules away from the membrane surface (Van den Berg and Smolders 1989a).

Table 1 presents a theoretical estimation of osmotic pressure in GDM ultrafiltration for two types of macromolecules with a molecular weight of 50 and 100 kDa, based on Morse equation (Eq. 3):

$$\Pi = i*M*R*T \qquad [atm] \tag{3}$$

where i=1 is dimensionless van't Hoff factor, M is molarity, R=0.08206 L atm K^{-1} mol^{-1} is the gas constant, T=273.15 is temperature, K. The van't Hoff factor depends on level of dissociation in water and is typically used for inorganic species (salts),

but can also be applied for macromolecules that do not dissociate, where its value is 1 or below.

If osmotic pressure limitations were important for GDM, they would be more visible for low molecular weight (MW) compounds (since osmotic pressure is related to MW of the retained solute) and close to the proximity of the membrane wall. In GDM project all experiments are carried out in so-called membrane biofouling monitors, with active membrane surface area of 0.0021 m^2 and effective distance between membrane surface and the biofouling monitor cover of 1.5 mm (1500 μm). If we took an average macromolecule concentration in surface water (creek, river) of 0.2 mg L^{-1} and filtered 1 L of water (which corresponds to around 5 days of continuous filtration), then we would obtain the macromolecules concentration at the membrane wall C_w 95 g macromolecules L^{-1}, assuming 100% retention of the molecules by the membrane.

Table 1 *Theoretical estimation of osmotic pressure in GDM ultrafiltration assuming that macromolecules (either 50 or 100 kDa) accumulate in a small volume near to the membrane surface. Accumulation of macromolecules will depend on advective transport towards the membrane and local diffusion away from the membrane. Concentrations and osmotic pressures are shown for 476.1 L m^{-2} filtered water and a macromolecule concentration in the feed of 0.2 mg L^{-1}, corresponding to 5 days of filtration.*

Assumed layer thickness of accumulating macromolecules, μm	Concentration of accumulated macromolecules near the membrane (C_w), g L^{-1}	Osmotic pressure Π for size of macromolecules in the influent, mbar	
		50 kDa :	100 kDa :
1	95,2	43,3	21,6
5	19,0	8,7	4,3
20	4,8	2,2	1,1
100	1,0	0,4	0,2
200	0,5	0,2	0,1
500	0,2	0,1	0,0
1000	0,1	0,0	0,0
1500	0,1	0,0	0,0

From Table 1 we can conclude that theoretically the highest osmotic pressure would be situated in the close proximity of the membrane wall, with osmotic pressure working against the transmembrane pressure (TMP range in GDM is typically 60-100 mbar). However, since in GDM we have both accumulation of macromolecules with different molecular weights (Huber et al. 2011) and biofilm growth (with macromolecules of higher molecular sizes between 500 – 2000 kDa (Flemming and Wingender 2010)), then it could be that both osmotic and true gel

(biofilm structure) models overlap at some point with respect to resistances. So far "the degree of organization of the EPS matrix, as random arrangements or specifically linked constituents, remains to be established" (Neu and Lawrence 2015). Thus a model yielding both osmotic and gel limitations in dead-end unstirred UF of aqueous bovine serum albumin (BSA) was proposed by Reihanian et al. (1983). In this model they hypothesized co-existence of a gel layer, which is not prone to back-diffusion (upon cessation of filtration) and an osmotic layer, which diffuses more readily back into the bulk. If these two models: osmotic and gel resistance model overlap in GDM, then in practice it could be difficult to correlate true biofilm structure with the flux, since if a polarisation layer (which is not readily measured) is disturbed and heterogeneous, then mass transfer through the membrane will also increase. Another challenge for the flux model in GDM would be on how to assume diffusivity D across the osmotic – biofilm model layers: constant, or variable, across the layer thickness. Yet without biodegradation of the large macromolecules, their accumulation at the membrane surface will lead to a progressive flux decline, whichever model we assume to dominate in GDM: osmotic or gel.

While the cake model (a) assumes linear resistance increase, the osmotic-gel model (b) assumes non-linear resistance increase due to gel layer development and maturation (Xiao et al. 2013), as well as transition between reversible (polarisation effects) and irreversible fouling due to liquid/solid transition at the membrane surface (Bessiere et al. 2005).

However, the two models (a) and (b) assume continuous increase of the resistances in the dead-end unstirred ultrafiltration in absence of biological activity, due to accumulation of the particles and macromolecules. It is not clear how biofilm presence could affect the resistance due to macromolecules accumulation and possible degradation, as well as production (biofilms are themselves composed of macromolecules, i.e., EPS).

In GDM filtration (c) the main resistance development is due to biofilm growth on the membrane surface. Due to the biofilm development the resistance does not increase with time, resulting in stabilisation of the permeate flux (Peter-Varbanets et al. 2011) despite continuous inorganic and organic matter accumulation. It seems that natural organic matter composition in feedwater determines the resistance and permeate flux (Jermann et al. 2008, Peter-Varbanets et al. 2011). Another parameter that strongly influences the level of flux stabilisation is biofilm structure and composition, i.e., presence of predators (Derlon et al. 2013, Derlon et al. 2012).

It is not known how the biofilm influences permeate flux and quality due to degradation capability of the organic matter, which would reduce the organic matter concentration in permeate, but at the same time increase biofilm mass. Also it is unknown how biofilm interacts with high concentrations of inorganic particles which cannot be degraded, but can accumulate and affect the biofilm structure and thus flux for long term filtration. Although short term filterability studies in membrane bioreactors have shown that addition of non-compressible particles can decrease biomass compressibility and increase flux (Teychene et al. 2011).

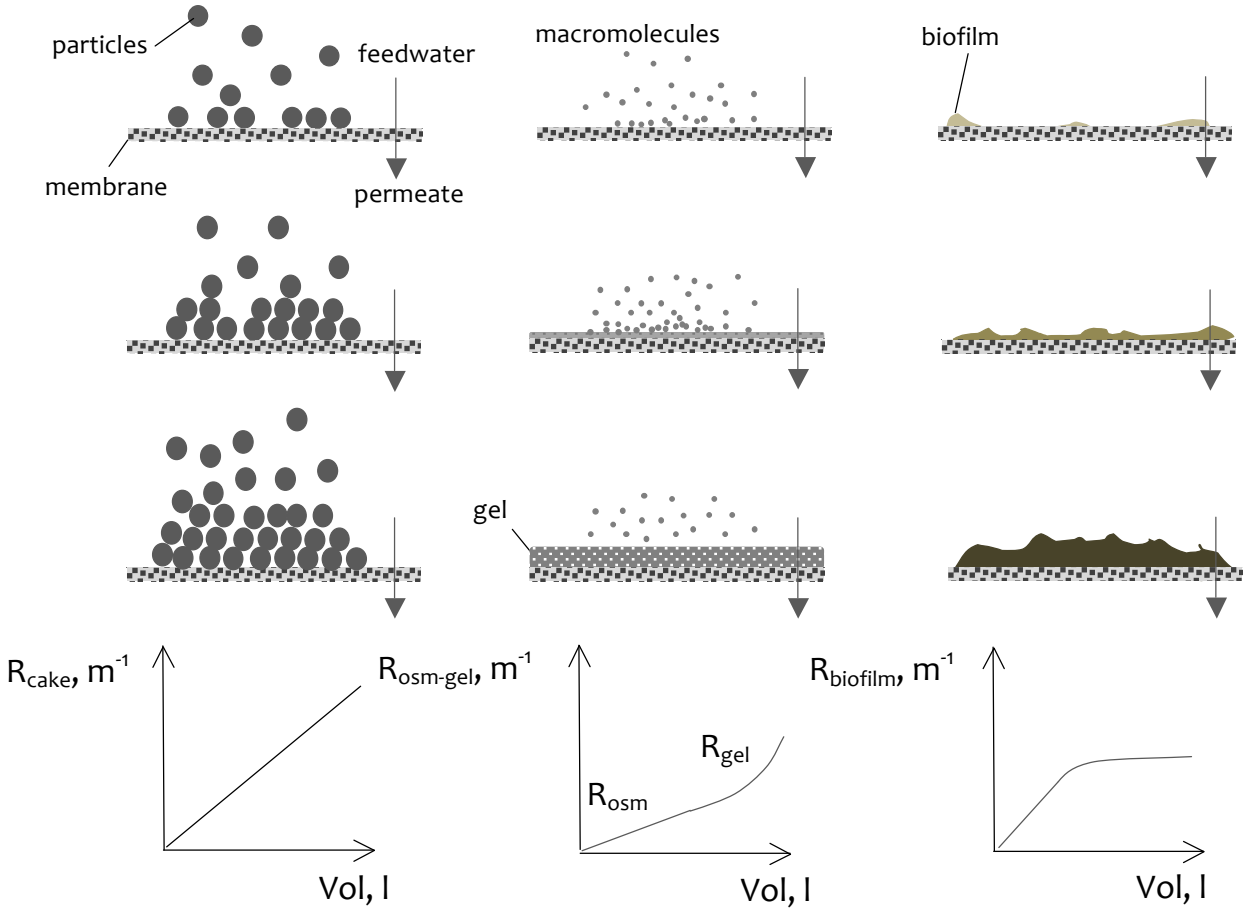

Figure 3 *Simplified resistance to filtration models: (a) R_{cake}: cake filtration (accumulation of inorganics) (b) $R_{osm-gel}$: osmotic-gel model (accumulation of macromolecules, such as proteins). The initial stage of macromolecules accumulation leads to a reversible layer with osmotic resistance, and later to an irreversible gel layer (Bessiere et al. 2005). The gel development and maturation leads to increased resistance (Xiao et al. 2013) (c) $R_{biofilm}$: GDM (gravity driven membrane) model, based on biofilm development. All models assume constant long term dead-end filtration, without shear.*

General objectives of the thesis

The overall objective of the thesis was to identify interactions between the biofilm development on ultrafiltration membrane and model inorganic and organic compounds that can be found in feedwater. The accumulation of inorganic matter can directly influence biofilm structure and in turn determine permeate quantity. The accumulation and permeation of organic matter can affect biofilm growth due to additional substrate load, also determining permeate quantity. At the same time biofilm presence allows for hydrolysis and degradation of the organics, influencing the permeate quality. The accumulation of inorganic and organic matter in GDM was studied separately, in both cases during biofilm development on the membrane surface.

The specific questions in this thesis were therefore:

How does the accumulation of inorganic particles influence the biofilm structure and in turn resistance to filtration? How do the specific resistances of the particle cake and biofilm relate? (**Chapter 2**)

How does accumulation or passage of degradable and non-degradable organic foulants affect biofilm growth and in turn resistance to filtration? How does the biofilm presence affect hydrolysis and uptake of the foulants and in turn permeate quality? Is it better to operate the system under constant or variable foulant loading? (**Chapter 3**)

How does biofilm accumulation and growth affect consumption and production of assimilable organic carbon, which influences permeate quality and stability with respect to bacteriological regrowth? Does biological pre-treatment help to increase stability of the produced permeate? (**Chapter 4**)

Significance of the work

Costs of membrane materials have decreased considerably over the years (AMTA 2007), for instance cost of UF submerged membrane modules dropped from 400 $ to less than 50 $ per m^2 membrane between years 1992 and 2005 (Baker 2012). With the membrane prices still decreasing (at a slower pace though than the last 15 years), or possibility to inexpensively obtain old, irreversibly, irrecoverably fouled membranes that are beyond high flux recovery (from industrial point of view), the "membrane – biofilm" composite becomes a new viable filtration approach, as opposed to membrane filtration only. Tolerating the presence of biofilm on

membrane surface can have a beneficial effect on the quality of produced permeate even if its quantity is decreased (Derlon et al. 2014). The thesis contributes to supporting this approach by investigating influence of model inorganic and organic foulants onto biofilm structure and activity (hydrolysis, degradation). The biofilm structure governs resistance to filtration and thus permeate flux, while the degradation ability by the biofilm strongly influences permeate quality. The mechanisms investigated show that presence of inorganic or organic foulants shapes biofilm structure and activity, and allows to understand when additional measures (like feedwater pre-treatment) would be beneficial for the overall GDM system. These mechanisms are currently explored for drinking water purposes, but should be expanded to grey water or wastewater.

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Chapter 2

Biofilm formation and permeate quality improvement in Gravity Driven Membrane ultrafiltration

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Minor modifications to the original paper have been made – all of the modifications are highlighted directly in the text *in italics* and marked with ***.**

Abstract

The effects of biofilm development on ultrafiltration membranes with regards to permeate stability and permeation rates were investigated using Gravity-Driven Membrane (GDM) filtration. The first part of the study aimed at evaluating the influence of the biofilm on permeate flux quality and quantity with regards to Assimilable Organic Carbon (AOC) degradation. In addition, two types of biological pre-treatments were evaluated: slow sand filtration and packed bed bio-reactor, compared to a control (no treatment). Biofilm formation helped to decrease the AOC content of permeate water, compared to the influent. Both pre-treatments additionally reduced AOC level in permeate and thus increased its biological stability, however none of the systems were able to guarantee microbiologically stable water. Removal of AOC before the GDM filtration reduced the biofilm growth potential, which in turn influenced its physical structure and enhanced the permeation rates.

Influence of inorganic particle removal by pre-sedimentation and its effect on the biofilm structure was also studied. Pre-sedimentation of particle populations selected fine and homogenous particle fractions, which lead to the formation of a homogenous biofilm structure characterized by an increased hydraulic resistance. This was clearly visible between horizontally and vertically installed membranes where the latter ones had a significantly reduced flux despite lower deposited particle mass. Presence of larger, heterogeneous particle fractions counterbalanced the negative effects of the fine particles, which overall resulted in enhanced permeation rates.

Keywords

assimilable organic carbon, biofilm structure, Gravity Driven Membrane ultrafiltration, permeate flux, pretreatment

Introduction

In conventional membrane filtration systems feedwaters are often pre-treated, with the aim to limit the amount of foulants entering the membrane system and thus reduce membrane fouling potential. Biofilms are often undesired in membrane processes, as they not only significantly reduce permeation rates, but can also negatively affect permeate quality (Flemming et al. 1997, Herzberg and Elimelech

2007). A different approach is used in low-pressure Gravity Driven Membrane (GDM) ultrafiltration, which uses gravity as the sole driving force for the filtration of surface waters, for potable water purposes, and that tolerates biofilm growth (Peter-Varbanets et al. 2010). During long term filtration the GDM membranes become biologically activated; the biofilm stabilises permeate flux and is not controlled nor removed during operation. Its biological activity eliminates the need for troublesome membrane cleaning and maintenance. Hence GDM is an attractive option for Point Of Use (POU) and decentralised water treatment, but the exact influences of the biofilm development with regards to permeate quality and stability remains unknown.

Assimilable Organic Carbon (AOC) is a conventional indicator of drinking water quality and stability, assessing the capacity of microbiological growth in the water, with different concentration values proposed to ensure microbiologically stable water: 10 µg L^{-1} (Van Der Kooij 1992), 20 µg L^{-1} (Lechevallier et al. 1993), 100 µg L^{-1} (Hammes et al. 2010). In conventional membrane treatment processes (reverse osmosis, ultrafiltration) the solute to potential biofilm contact time is in the order of seconds (often due to crossflow mode of filtration), and thus degradation of AOC *which would lead to significant permeate quality improvement** is not expected. In GDM system, with thicker biofilms, the solute to biofilm contact time is in order of minutes. It is thus hypothesized that due to longer contact times significant AOC degradation can occur during GDM filtration, resulting in an increased permeate quality, as proposed by Zhang and Huck (1996) for biological water treatment processes.

Biodegradable solute fractions significantly affect membrane fouling and thus govern permeation rates in low pressure membrane filtration (Filloux et al. 2012, Peter-Varbanets et al. 2011). Soluble solute, such as AOC, can in addition permeate through virgin ultrafiltration membrane and deteriorate permeate water quality. Favourably, simple biological pre-treatment steps can be applied to enhance removal of AOC prior to membrane filtration (Halle et al. 2009, Hammes et al. 2010). Therefore if AOC retention is increased prior to the GDM filtration system, not only more permeable biofilm should develop on the membrane surface, but the stability of permeate should improve. It is not known if biofiltration processes used to remove organic compounds from surface waters (Graham 1999, Halle et al. 2009, Peldszus et al. 2011) are suitable to enhance the GDM filtration performance, both in terms of permeate quality (potential of bacterial regrowth) and its quantity.

In large membrane systems operated at high transmembrane pressures a reduction in inorganic particle load is also practiced, i.e. by particle sedimentation or cartridge pre-filtration. Such pre-treatment reduces the total amount of particles but may lead to a selection of fine, homogenous fractions, which can result in increased resistance to filtration (Fane 1984, Kim and Ng 2007). On the other hand, presence of larger particles can be beneficial, acting as a secondary membrane and capturing smaller particles to reduce the fouling potential of the primary membrane (Kuberkar and Davis 2000). Addition of inorganic particles also helped to improve performance of a membrane bioreactor during supernatant filtration (Teychene et al. 2011). It is unknown if presence of larger particulates can counterbalance the increased hydraulic resistance (Carman 1938) of biofilms in the GDM system.

The specific objective of this study was to evaluate the potential of biofilms growing on the membrane surface and additional biological pre-treatment on the reduction of AOC in the permeate (Experiment 1). The second objective was to evaluate how variation of the amount and composition of inorganic particles in the feedwater can influence the biofilm physical structure and in turn shape its permeability (Experiment 2).

Material and methods

Experimental set up

Experiment 1: Biological pre-treatment and regrowth potential

Three systems were operated in parallel: GDM control, PBBR+GDM and SSF+GDM system. Each system was composed of a water tank connected to 4 biofouling monitors (Figure 1).

The GDM control received untreated feed water. The PBBR+GDM and SSF+GDM systems were equipped with a pre-treatment: a Packed Bed Biofilm Reactor (PBBR) or a Slow Sand Filter (SSF). In order to compare the performance of the installed pre-treatments, each pre-treatment had an equal residence time of 60 minutes. The SSF depth was 60 cm, of which 5 cm bottom support was 12 mm gravel, followed by 5 cm of 6 mm gravel and top 50 cm of sand layer (diameter = 0.3 - 0.5 mm). The PBBR depth was 50 cm, packed with plastic carriers type BWT 15 (Biowater Technology, Tonsberg, Norway), with protected surface 828 m^2/m^3. The carriers were inoculated with tap water for one month. Pre-treatment reactors were not aerated since the creek river water was carbon limited (oxygen saturation level was

measured). More details of the pre-treatment systems are given in the Supplementary information. Feed water was pumped to a completely mixed tank and controlled to 20°C. Afterwards, it was distributed to each system (at different flow rates in order to keep similar retention times). The water tanks were placed at a height corresponding to a transmembrane pressure of 70 mBar. Permeate of each biofouling monitor was collected in bottles and weighed daily.

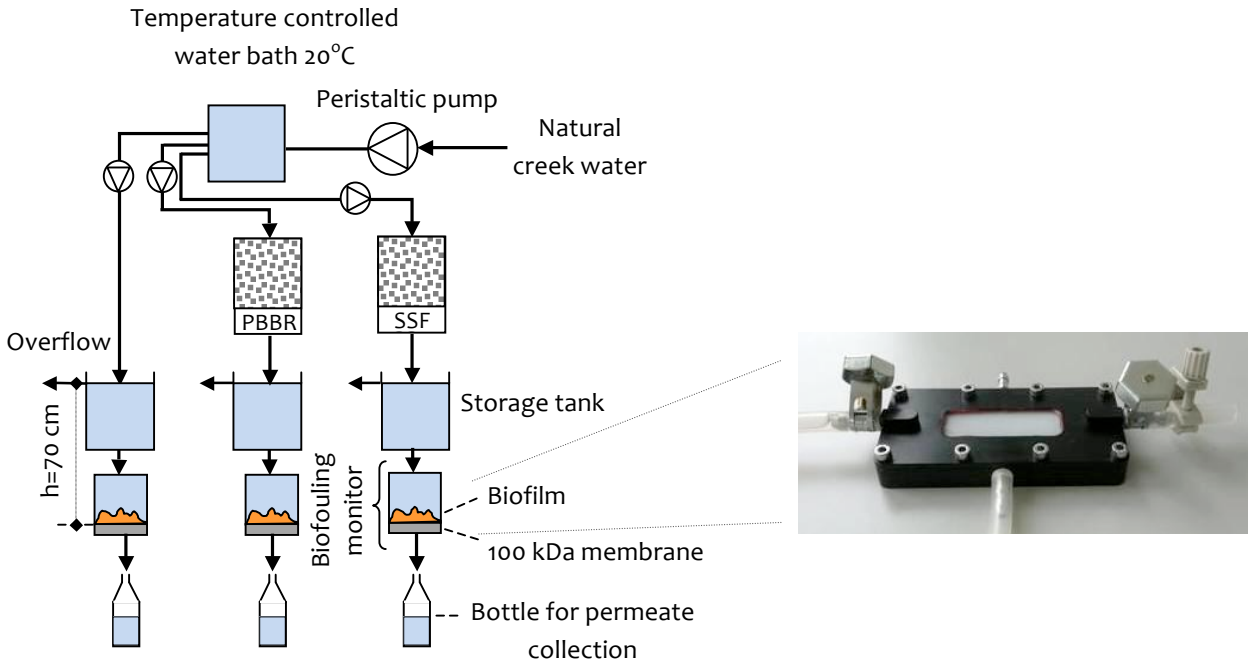

Figure 1 *Schematic layout of the Experiment 1 setup (left) with the biofouling monitor (right).*

Experiment 2: Inorganic particle pre-treatment

Two experiments were conducted with regards to particle addition:

2A: filtration of creek water with particle pre-coated membranes;
2B: filtration with continuous addition of particles, with pre-filtered creek water

In experiment 2A each membrane was initially pre-coated with a defined mass of particles (summarised in Table 1). The experiment was conducted with use of 48 mm diameter Whatman (Maidstone, Kent, UK) polycarbonate filter holders, and three membranes were used per each condition.

Table 1 *Particle mass and characteristics for experiment 2A.*

Condition	Pre-coat mass, g
Control	-
Kaolin d_{50} = 3.8 µm	1
Diatomaceous earth d_{50} = 21.9 µm	1
Fine sand 0.25-0.4 mm	2
Sand <0.63 mm	2

In experiment 2B, two fine particle fractions were being added continuously (to a freshly pre-filtered river water, ultrafiltration membrane 150 kDa, Microdyn Nadir, Germany) at a concentration of 300 mg L^{-1}: kaolin (d_{50}=3.8 µm), and kaolin with diatomaceous earth mix (d_{50}=18.0 µm), 50/50%, by mass. The experiment was conducted in a tank divided into three compartments (12 L each, HRT of each compartment ± 11.5 days); of which two were used for the continuous addition of particles (allowing for their natural dispersion and sedimentation onto the installed membranes), one for control (no addition). Each compartment had vertically and horizontally installed membrane holders, and at least three membranes were used per each condition. In both experiments 2A and 2B a transmembrane pressure of 55 mBar was used, temperature was controlled to 20°C, and permeate was collected in bottles and weighed regularly. The feed waters were being mixed in dosing tanks and fed separately into the respective tank compartments via peristaltic pumps (details in Figure 2).

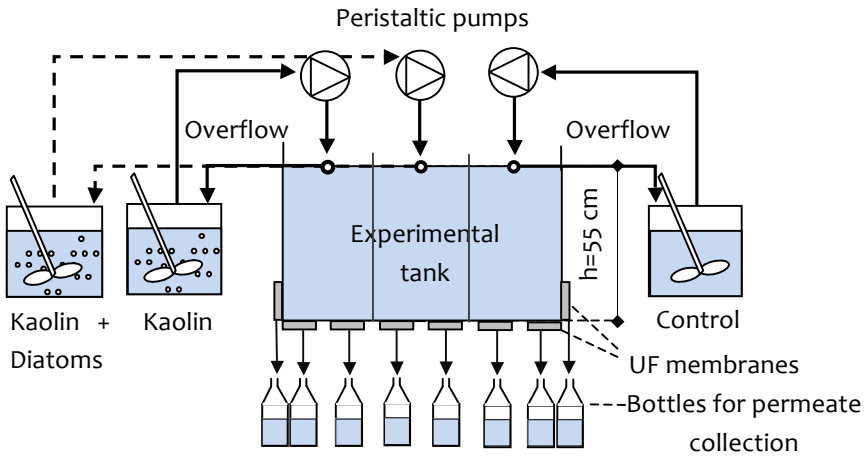

Figure 2 *Schematic layout of the Experiment 2 setup.*

Membrane

Polyethersulfone membranes (Microdyn Nadir, Wiesbaden, Germany) with a nominal cut-off of 100 kDa were used (mean pore size: 10 nm) in the experiments. To remove conservation agents membranes were flushed and stored for 24 h in deionised water. Permeability tests were conducted with deionised water to ensure integrity of the membranes and their comparable permeability level - all membranes with a standard deviation of initial permeability larger than 15% were discarded.

For experiment 1, membranes were placed in specifically designed biofouling monitors (membrane surface 0.00149 m^2), suitable for monitoring of the biofilm

structure in situ. For experiment 2, membranes were placed in filter holders (membrane surface 0.00159 m^2). All membranes were operated continuously in dead end mode, without flushing or cleaning.

Water characterisation

Dissolved and Total Organic Carbon (DOC, TOC)

All experiments were performed with creek river water, characterised by a Total Organic Carbon (TOC) level of 3.3 ± 0.8 mg L^{-1} (SD) and a Dissolved Organic Carbon (DOC) level of 2.7 ± 0.6 mg L^{-1}. TOC and DOC were measured with a total organic carbon analyzer (TOC-V, Shimadzu, Japan).

Assimilable Organic Carbon (AOC)

Assimilable Organic Carbon (AOC) was measured to assess regrowth potential (Hammes and Egli 2005) in the feed water, in the effluent of the pre-treatments and in the permeate of the tested systems. Triplicate samples of each water sample were filled into sterile carbon-free vials. Samples were then inoculated with 1000 µL of natural microbial community and incubated for 3 days at 30°C. Total cell concentrations of the indigenous microbial community were determined using flow cytometry (Partec, Cyflow2, Germany). The net-growth was used as an indicator of the AOC concentration left in the sample according to the conversion rate of 1 µg AOC mL^{-1} = 1 x 10^7 cells mL^{-1} (Hammes and Egli 2005). Hence AOC is a small fraction (up to 20%) of the creek water DOC, this parameter was selected as meaningful to assess the biological regrowth potential.

Inorganic particles

Inorganic particles stability against aggregation over time (experiment 2B) was confirmed by particle size time series measurements (Mastersizer 2000, Malvern Instruments, UK). Suspensions of the particles were prepared in pre-filtered river water and their size distribution was measured over a 2 day period. It was confirmed that the prepared solutions were stable against aggregation over 48 hr period. Hence feed water solution was freshly prepared every 2 days.

Biofilm physical structure characterisation

Mesoscale level

Optical Coherence Tomography (OCT) (model 930 nm Spectral Domain, Thorlabs GmbH, Dachau, Germany) with a light source wavelength of 930 nm was used to investigate the meso-scale structure of the biofilm. Imaging procedure and image analysis was done as described by Derlon et al. (2012).

Microscale level

A Scanning Electron Microscope (SEM; Nova NanoSEM 230 FEG, FEI Inc., Oregon, USA) was operated in low vacuum mode to image biofilm structure at microscale level. No sample coating or alteration was employed, as the instrument allowed for direct observation using a VCD (Variable Contrast Detector). The images allowed for biofilm heterogeneity determination (by ImageJ software), using Plot Profile function, which analyses pixel intensity distribution of the selected image cross-sections. Two cross-sections from each SEM image were used to determine biofilm heterogeneity in Experiment 2A.

Total solids and volatile solids measurements

Biomass (volatile solids) and total solids mass were determined at the end of the experiment 2B, following Standard Method (APHA 2005).

Results and discussion

Exp. 1: Effect of biological pre-treatment on removal of AOC and permeate stabilization

Improvement in biological stability of permeate water was monitored during 244 days of continuous filtration. Significant AOC degradation was observed for each system stage (pre-treatment, membrane), which is seen as a difference in concentration of AOC in the inlet and outlet of the stages (Figure 3).

The mean influent AOC concentration was 411 ± 337 µg L^{-1} (SD) and significant AOC degradation was achieved by the pre-treatment, with removal efficiencies of 79% by SSF (85 ± 37 µg L^{-1} of AOC in the outlet of SSF) and 70% by PBBR (125 ± 41 µg L^{-1} of AOC in the outlet of PBBR). Large standard deviations of AOC concentration are due to seasonal variability in the creek river water composition (i.e. rain, thaw).

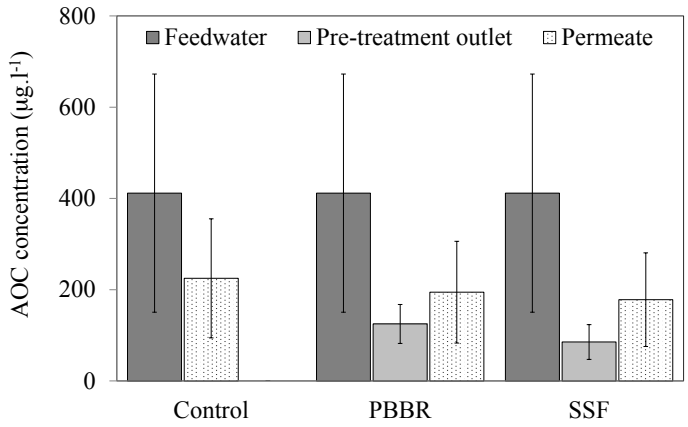

Figure 3 *Mean AOC concentrations of the three systems studied: control – GDM with creek river water without pre-treatment; PBBR – GDM with packed bed bioreactor as pre-treatment; SSF – GDM with slow sand filter as pre-treatment.*

In terms of overall permeate quality, introduction of a pre-treatment before the GDM system improved its stability (178 ± 99 µg L^{-1} of AOC and 195 ± 108 µg L^{-1} AOC for SSF and PBBR system, respectively), however the values obtained are above the limits proposed for microbiologically stable water of: 10 µg L^{-1} (Van Der Kooij 1992), 20 µg L^{-1} (Lechevallier et al. 1993), 100 µg L^{-1} (Hammes et al. 2010). After the membrane the AOC content increased (observed from the pre-treatment outlet to the GDM system outlet), which is probably related to hydrolysis processes occurring within the biofilm formed on the membrane surface. In SSF the top layer (i.e. the schmutzdecke) is followed by significant passage through the sand bed. If soluble compounds are produced in the schmutzdecke due to hydrolysis of organic matter, they can however be degraded in the subsequent sand bed. In the GDM module the biofilm on the membrane surface is similar to the schmutzdecke, *with active biofilm located in the thin layer (200-300 µm), which is comparable with the thin (few mm) active layer in the slow sand filter*.* But the soluble compounds released by this biofilm are then not degraded due to the absence of subsequent active zone and thus deteriorate the permeate quality.

Introduction of pre-treatment processes before the GDM module reduced AOC and turbidity levels reaching the membrane surface, resulting in limited biofilm development. Biofilm development consists of active growth on substrate (AOC) and particulate matter accumulation (turbidity). Pre-treatment steps reduced both AOC and turbidity levels, which resulted in the thinnest biofilm development in the GDM+SSF system, followed by the GDM+PBBR, and the thickest in GDM control (seen in Figure 4).

The cumulative AOC values (Fig. 5B; acquired by multiplying cumulative permeate volumes with the average AOC concentration from each system) obtained at the end of the experiment were 135 µg AOC m^{-2} and 106 µg AOC m^{-2} for the GDM systems equipped with PBBR and SSF, respectively, compared to 397 µg AOC m^{-2} for the control (corresponding to 66 and 73% AOC load reduction, respectively). The AOC load correlated with the biofilm thickness development, as shown in Figure 4.

The biofilm thickness furthermore corresponded with the achieved permeation volumes (highest in the SSF, lowest in the control system), which are depicted in Figure 5A.

The cumulative permeate volumes obtained an the end of the experiment were 1084 L m^{-2} and 1243 L m^{-2} for the GDM systems containing PBBR and SSF as a pre-treatment, respectively. This compares with 966 L m^{-2} for the control (corresponding to the relative values of 112 and 129% for PBBR and SSF, respectively). In our case the differences in permeation rates could be directly associated with the thickness of the biofilm, however correlating biofilm structure with permeation rates requires more parameters (i.e. biofilm relative roughness coefficient), as demonstrated by Derlon et al. (2012) and Peter-Varbanets et al. (2011).

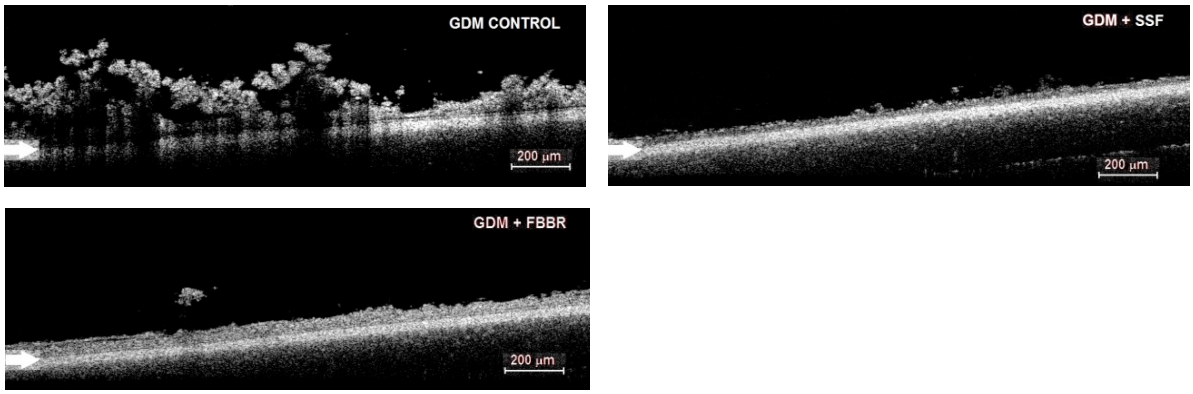

Figure 4 *Thickness of the biofilm formed on the membrane surface for each system, imaged by OCT (day 76). GDM control - without pre-treatment; GDM+PBBR - GDM with packed bed bioreactor; GDM+SSF – GDM with slow sand filter. The white arrows indicate the membrane surface.*

A B

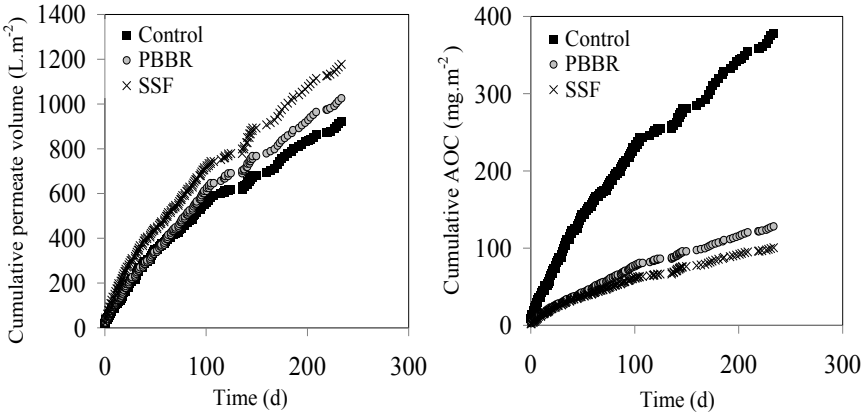

Figure 5 *Differences in permeate volumes between the three systems (A), and corresponding cumulative values of AOC reaching the membrane surface (B) for: control - GDM (without pre-treatment) PBBR – GDM with packed bed bioreactor as pre-treatment; SSF – GDM with slow sand filter as pre-treatment.*

Exp. 2: Effect of inorganic particle pre-treatment on biofilm structure and filtration resistance

Mean permeate flux values of the experiments 2A (with initial membrane pre-coating) and 2B (continuous addition of the particle fractions) are shown in Figure 6. In both experiments the finest particle fraction (kaolin, d_{50}=3.8 µm) most negatively affected the permeate flux. For experiment 2A, obtained permeation rates were 7.7 ± 0.8 L m^{-2} h^{-1} (control), compared to 3.7 ± 0.3 L m^{-2} h^{-1} (kaolin), which corresponds to around 50% flux reduction. Diatoms and sand fractions did not offer significant resistance to filtration and thus did not influence the permeation rates (fluxes of: 6.4 ± 0.4 L m^{-2} h^{-1} for diatoms, 6.5 ± 0.5 L m^{-2} h^{-1} for sand 0.25-0.4 mm, 7.3 ± 0.6 L m^{-2} h^{-1} for sand <0.63 mm).

For continuous particle addition (experiment 2B), presence of diatoms (d_{50}=21.9 µm) in the horizontal membrane configuration counterbalanced the negative effects of kaolin particles, and the respective permeation rates of 7.6 ± 0.2 L m^{-2} h^{-1} for control, 4.2 ± 0.8 L m^{-2} h^{-1} for kaolin, and 7.4 ± 0.2 L m^{-2} h^{-1} for the kaolin and diatoms mix were achieved. In the vertical membrane configuration, where the diatoms settled out and did not reach the membrane surface, reduced permeation rates were obtained: 8.1 ± 0.3 L m^{-2} h^{-1} for control, 5.3 ± 0.4 L m^{-2} h^{-1} for kaolin, and 5.4 ± 0.3 L m^{-2} h^{-1} for the kaolin and diatoms mix (Figure 6). Furthermore, accumulation of kaolin (in Fig. 6 Horizontal) resulted in progressive flux decline and no final flux stabilisation, which is represented by an increased standard deviation (compared to the other experimental conditions).

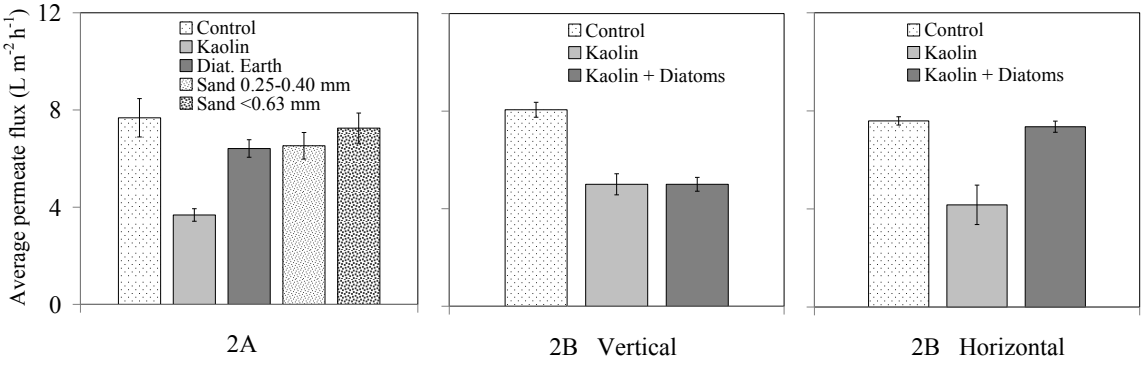

Figure 6 *Permeate flux values from the flux stable period of the particle pre-coated membranes (2A) during dead-end filtration of creek river water, compared to continuous particle addition filtration (2B), performed in two membrane configurations: horizontal and vertical. Each error bar indicates standard deviation.*

Biofilm thickness correlated with accumulated mass on the membrane surface, with significantly more accumulated mass in the horizontal membrane configuration (experiment 2B, Table 2). The horizontal and vertical membrane arrangement determined the amount of accumulated mass; however this parameter itself did not determine the biofilm permeability. Despite a significantly thicker biofilm in the horizontal membranes, presence of the heterogeneous particle populations (diatoms) created more heterogeneous and thus more permeable biofilm structure, which ensures flux stabilization at a high level.

Table 2 *Volatile and total solids measured from the cake layer removed at the end of experiment 2B, compared with the biofilm thickness (measured by OCT). HOR - horizontal, VER - vertical membrane configuration.*

Condition	TS, g	VS, g	Biofilm thickness, μm
Control HOR	0.037	0.035	284 ± 43
Control VER	0.007	0.005	71 ± 5
Kaolin HOR	1.252	0.159	1862 ± 86
Kaolin VER	0.084	0.011	313 ± 33
Kaolin + Diatoms HOR	1.006	0.083	1696 ± 98
Kaolin + Diatoms VER	0.097	0.019	322 ± 55

For populations of particles (found in natural waters), the highest cake resistances come from their smallest size fractions, as demonstrated by Carman (1938) and Kim and Ng (2007). In our experiment (2A) kaolin particles of size up to 1 μm represented 13% of the overall particle distribution, while for diatomaceous earth this value was only 1.7%. For the particle class size up to 2 μm, these values doubled to 26% for kaolin, and to 3% for the diatoms. Natural particle pre-sedimentation

within the experimental tank occurred (Exp. 2B), which prevented the larger particle fractions (diatoms) from reaching the vertical membranes and in turn negatively affected the permeation rates.

SEM micrographs (Figure 7) taken at the end of experiment 2A captured biofilm structural differences and allowed to determine its heterogeneity (corresponding greyscale pixel intensity distribution is shown below the SEM images). Since the original SEM micrographs do not have the same greyscale threshold values, this method allowed for determination of deviations of greyscale distribution, which can be used as an indicator of biofilm heterogeneity. Visually, homogenous particle fractions (kaolin) created a homogenous biofilm structure (Fig. 7A), while a heterogeneous particle population (diatoms) produced a heterogeneous one (Fig. 7B). This is supported by the pixel greyscale distribution, with almost a triple greyscale standard deviation for the diatoms (84 ± 22), compared to the standard deviation of kaolin (73 ± 8).

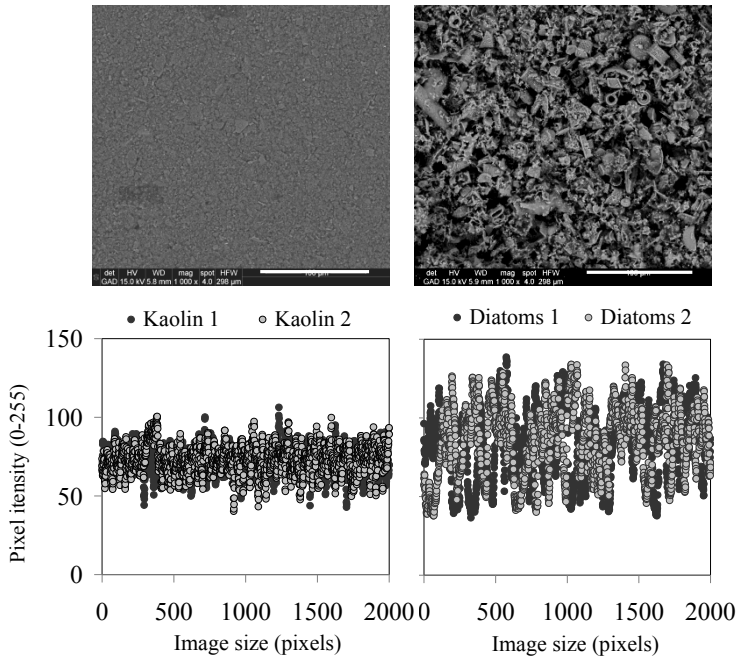

Figure 7 *Top view SEM micrographs of biofilm structure formed in the presence of kaolin (A) and diatomaceous earth (B), from Experiment 2A. Image size area 300 x 300 µm.*
The corresponding biofilm heterogeneity (based on greyscale pixel intensity distribution of SEM micrograph) is shown below. Diatomaceous earth greyscale distribution shows a significantly increased deviation of the average pixel distribution, compared to kaolin particles.

Conclusions

Biological pre-treatment (such as PBBR and SSF) of feed water may enhance the quality and the quantity of the drinking water provided by the GDM filtration system, while physical separation of inorganic particles (e.g., by sedimentation) can be detrimental in terms of permeation rates reduction for the GDM ultrafiltration systems.

Biofilms growing on ultrafiltration membranes increase permeate quality by reducing the feed water AOC content, however the quality of permeate still cannot be considered as stable. Over long term (several months) permeate quality decreases due to hydrolysis processes within the biofilm, releasing soluble organic carbon, which requires further detailed study at both mesoscale and microscale levels.

Pre-treatment of the creek river water (PBBR or SSF) is a suitable approach to favour the formation of biofilms associated with reduced AOC load and therefore limited growth potential, thus helping to maintain a higher permeate quality. However, the main advantage is the increase in the quantity of the permeate water. In order to achieve a higher stability of the drinking water, it may be better to implement an additional biological post-treatment instead of pre-treatment.

Pre-sedimentation of inorganic fractions selects finest homogenous particles that offer increased resistance to filtration. Presence of larger, heterogeneous particles (that sediment onto horizontal membrane configuration) can counterbalance the negative effects of fine particles selected in the vertical membrane configuration. Thus heterogeneous biofilm is created with lower resistance to filtration. In case of turbid raw waters, particle pre-sedimentation may actually reduce the permeation rates due to removal of heterogeneous fractions (compared to untreated water and to control, without particles).

Additional information on reactor parameters and composition of the river water used in the experiment is given in the Supplementary information.

Abbreviations

AOC	Assimilable Organic Carbon
DOC	Dissolved Organic Carbon
FEG	Field Emission Gun
GDM	Gravity Driven Membrane
HRT	Hydraulic Retention Time
kDa	kilo Dalton
MW	Molecular Weight
OCT	Optical Coherence Tomography
PBBR	Packed Bed Bioreactor
POU	Point Of Use
SD	Standard Deviation

SEM	Scanning Electron Microscopy
SSF	Slow Sand Filter
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
TS	Total Solids
VCD	Variable Contrast Detector
VS	Volatile Solids

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SUPPLEMENTARY INFORMATION

Experiment 1: Biological pre-treatment and regrowth potential

Table 1 *Comparison of the reactor and operating parameters between control, SSF and PBBR.*

Setup characteristics	GDM Control	FBBR + GDM	SSF + GDM
Empty bed volume (L)	2.3	5.2	4.8
Residence time in pre-treatment (min)	-	60	60
Total residence time (min)	124	98	151
Velocity through media (m h^{-1})	-	0.318	0.133

Table 2 *Turbidity levels of the creek water, control and effluents of SSF and PBBR (standard deviation in brackets).*

Sample	Turbidity, NTU	Number of samples
Creek water [(1)]	5.6 (4.3)	36
Control [(2)]	4.5 (6.8)	32
PBBR outlet [(3)]	1.1 (0.7)	32
SSF outlet [(3)]	0.4 (0.2)	32

(1) measured in the water bath with temperature control

(2) measured in the control storage tank

(3) measured directly in the respective pre-treatment outlet

Experiment 2: Inorganic particle pre-treatment

Table 3 *Total and Dissolved Organic Carbon of the feed and permeate waters (standard deviation in brackets).*

Control	TOC (mg L^{-1})		DOC (mg L^{-1})	
Feedwater	2.6	(0.4)	2.5	(0.4)
Permeate HOR	2.5	(0.4)	2.5	(0.3)
Permeate VER	2.6	(0.3)	2.6	(0.3)
Kaolin				
Feedwater	2.6	(0.4)	2.6	(0.4)
Permeate HOR	2.5	(0.4)	2.5	(0.4)
Permeate VER	2.5	(0.4)	2.5	(0.4)
Kaolin + Diatoms				
Feedwater	2.4	(0.4)	2.4	(0.4)
Permeate HOR	2.5	(0.4)	2.4	(0.4)
Permeate VER	2.7	(0.4)	2.6	(0.4)

Chapter 3

Inorganic particles increase biofilm heterogeneity and enhance permeate flux

This chapter has been published as:

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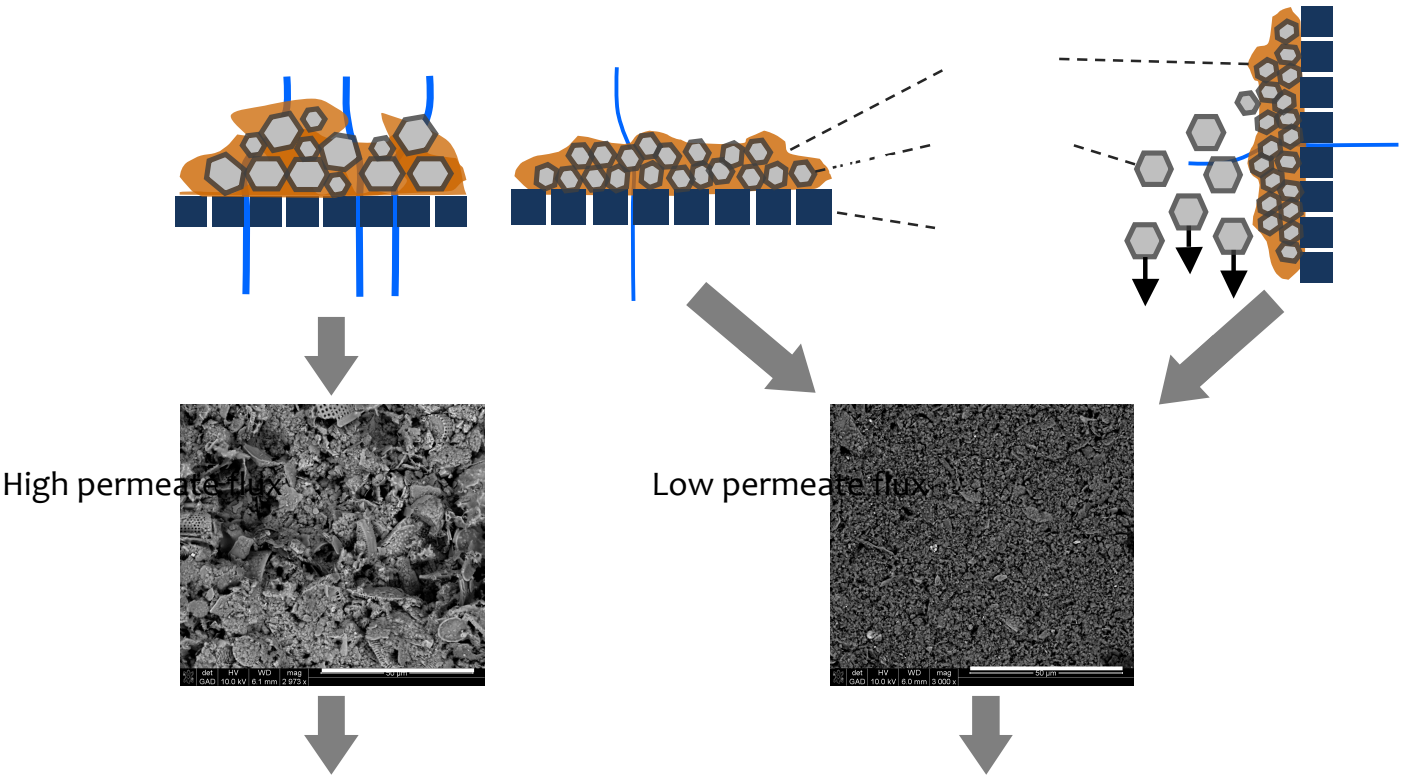
Minor modifications to the original paper have been made – all of the modifications are highlighted directly in the text *in italics* and marked with ***.**

Graphical abstract



Abstract

This study investigated the influence of inorganic particles on the hydraulic resistance of biofilm grown on membrane surface during low pressure dead-end ultrafiltration. Gravity-driven ultrafiltration membrane systems were operated during several weeks without any flushing or cleaning. Smaller (kaolin $d_{0.5}$ = 3.6 µm) or larger (kaolin with diatomaceous earth 50/50%, $d_{0.5}$ = 18.1 µm) particles were added to pre-filtered creek water or to unfiltered creek water. It was demonstrated in both experiments that presence of finer particles in the feed water (kaolin) induced formation of compact and homogeneous biofilm structure. On the other hand presence of the larger particles (diatoms) helped to counterbalance the effect of fine particles due to the formation of more heterogeneous and permeable biofilm structure. The hydraulic resistance of biofilms formed with fine particles was significantly higher than the resistance of biofilm formed in (1) absence of any inorganic particles or (2) in presence of the mixed particle population. The membrane orientation (vertical or horizontal) determined which particles were accumulating at the membrane surface, with structural differences shown by Scanning Electron Microscopy (SEM). For vertical membranes, the larger particles were selectively removed due to sedimentation and did not contribute to the biofilm development. Thus the selection of smaller particles due to vertical membrane configuration negatively affected the biofilm structure and permeation rates, and such selective accumulation of fine particles should be avoided.

Keywords

biofilm structure, cake resistance, particle size, permeate flux, gravity driven membrane (low pressure) ultrafiltration

Introduction

Cake formation due to particle deposition is a major problem in membrane systems. Cake formation is associated with reduced permeate flux. Different strategies are applied to limit the negative effects of particle deposition and to maintain high permeate fluxes, e.g., feed water pre-treatment or high cross-flow during filtration. Gravity-driven membrane (GDM) filtration is applied to the decentralized production of drinking water (point-of-use systems) (Peter-Varbanets et al. 2009). GDM filtration is performed in dead-end mode, without cross flow, without control of the biofilm formation, and typically without pre-treatment (Peter-Varbanets et al. 2010). Thus, cake formation in GDM filtration cannot be avoided using conventional approaches. However it is not clear to what extent particle deposition influences membrane flux by influencing specific resistance of the biofilm that forms on the membrane during GDM filtration.

Different strategies can be applied to control particles deposition. One approach is to pre-filter feed water to remove particles using, e.g., bag or cartridge pre-filtration devices (Huang et al. 2009). Such pre-treatment reduces the overall particle loading. But on the other hand it changes the size distribution and increases the fraction of fine particles that deposit on the membrane (Li et al. 1998). Ultimately, a cake with smaller porosity and higher specific cake resistance forms (Carman 1938, Kim and Ng 2007). Another approach to control particle deposition is to apply cross-flow conditions. But cross-flow conditions also promotes the deposition of small particles on the membrane while large particles are more likely to be removed (Li et al. 1998). Thus cakes formed under cross-flow conditions may have higher specific cake resistances than cakes formed in the dead-end filtration (Le-Clech et al. 2006). It remains unclear how the removal of large particles and in turn the selection of fine particles is beneficial or detrimental for the operation of the system.

Large particles in the feed water can also be beneficial to filtration. Larger particles that accumulate on the membrane surface can act as a secondary membrane layer that captures smaller particles and reduces the fouling potential of the primary membrane (Arora and Davis 1994, Kuberkar and Davis 2000). It has in fact been suggested that the addition of inorganic particles into the feed water can help to control membrane fouling in membrane bioreactors (Teychene et al. 2011). The added particles improved performance of the membrane bioreactor during supernatant filtration due to formation of a non-compressible fouling cake. However, previous studies (Arora and Davis 1994, Kuberkar and Davis 2000,

Teychene et al. 2011) were performed over short term (several hours) and/or under shear conditions, and most importantly: with suppression of biofilm growth on the membrane surface.

During GDM filtration the cake developing on the membrane is not just particles from the feed water but also a biofilm that grows on soluble substrates and products of hydrolysis. The activity of the biofilm in GDM filtration allows for long-term operation (months) of the system at a stable permeate flux. Similarly to permeable bio-barriers (Baveye et al. 1998), the total permeability in GDM results from both the biofilm growth and the particles presence. Accumulation of the particles could have both positive effects (by preventing biofilm densification) as well as negative ones (adding additional hydraulic resistance to water flow). However, the contribution of the inorganic particles to the development of the biofilm structure in low pressure ultrafiltration is unclear.

The aim of this study was therefore: (1) to evaluate how the presence of inorganic particles in the feed water influence the hydraulic resistance of biofilms developed during gravity-driven membrane ultrafiltration, (2) to understand how the configuration of the membrane (horizontal or vertical) influences the formation of the biofilm and in turn the system performance, and (3) to determine whether it is beneficial to pre-sediment the particles prior to the filtration. For this purpose gravity-driven systems equipped with horizontal (HOR) and vertical (VER) ultrafiltration membranes were operated in dead end-mode (no cross-flow), in the presence or absence of selected inorganic particles. The influent was augmented either with kaolin (=small particles), or with a mixture of kaolin and diatoms (50/50%, by mass), and compared to control (no particle addition). Kaolin represented non-settleable (under experimental conditions) particles, while diatoms represented the settleable particles.

Materials and methods

Experimental conditions and set up

Two long-term filtration experiments with biofilm growth and continuous-addition of particles were conducted (Table 1). Experiment A was conducted with pre-filtered (to remove larger organisms, natural particles and colloids) creek water and experiment B was performed with unfiltered creek water. Experiments A and B were performed in two membrane arrangements (HOR, VER). In these two experiments biofilms developed on the membrane surface and thus contributed to

the permeate flux reduction. In addition, a short-term experiment was conducted with deposition of inorganic particles on the membrane surface but without biofilm growth (Table 1, experiment C). During experiment C, the flux reduction resulted only from the formation of an inorganic cake and was not influenced by the biofilm development.

Table 1 *Summary of the experimental conditions with inorganic particle size distribution: biofilm growth due to bacterial growth (with 150 kDa membrane pre-filtered water A), biofilm growth due to bacterial growth and predation (unfiltered water B).*

Experiment	Duration	Condition	Membrane arrangement	Particle concentration mg L^{-1}	$d_{0.1}$ µm	$d_{0.5}$ µm	$d_{0.9}$ µm	Expected results
(A) prefiltered water	Long term (several weeks)	• Control • Kaolin • Kaolin + Diatom. earth	HOR, VER	• - • 300 • 150 + 150	• - • 0.9 • 2.9	• - • 3.6 • 18.1	• - • 9.3 • 45.0	$R_{biofilm}$ governed by particle accumulation + bacterial growth on substrate
(B) unfiltered water	Long term (several weeks)	• Control • Kaolin • Kaolin + Diatom. earth	HOR, VER	• - • 300 • 150 + 150	• - • 0.9 • 2.9	• - • 3.6 • 18.1	• - • 9.3 • 45.0	$R_{biofilm}$ governed by particles accumulation, bacterial growth on substrate and predation
(C) deionised water	Short term (several hours)	• Kaolin • Kaolin + Diatom. earth	HOR					R_{cake} due to inorganic particle accumulation

Experiments A and B were conducted using three identical tanks (Fig. 1), with a volume of 12 L each. Each tank was equipped with vertically and horizontally installed membrane holders (of equal membrane area of 0.00159 m^2). Two tanks were used for the continuous addition of particles (allowing for their natural dispersion and sedimentation onto the installed membranes), one for control (no particle addition). Suspensions of kaolin or kaolin with diatoms were separately added to tanks 1 and 2 (at a feed concentration of 300 mg L^{-1}), while tank 3 was used as control (no addition). The particle suspensions were stirred continuously in mixing tanks, and pumped into the experimental tanks using peristaltic pumps (Heidolph, Schwabach, Germany). An overflow was used to keep a constant water level of 55 cm (corresponding to a transmembrane pressure of 55 mBar). Experiments were performed at 20°C, with permeate collected in bottles and weighed regularly.

Experiment C was conducted by filtering deionised water through membranes (area 0.00159 m^2) evenly pre-coated with 1 gram of kaolin, or with 1 gram of

kaolin/diatoms mix (50/50%), at 20°C. The permeate flux was measured online at constant pressure of 55 mBar, over a period of at least 30 minutes, with balances connected to a PC. Three membranes were used per condition tested.

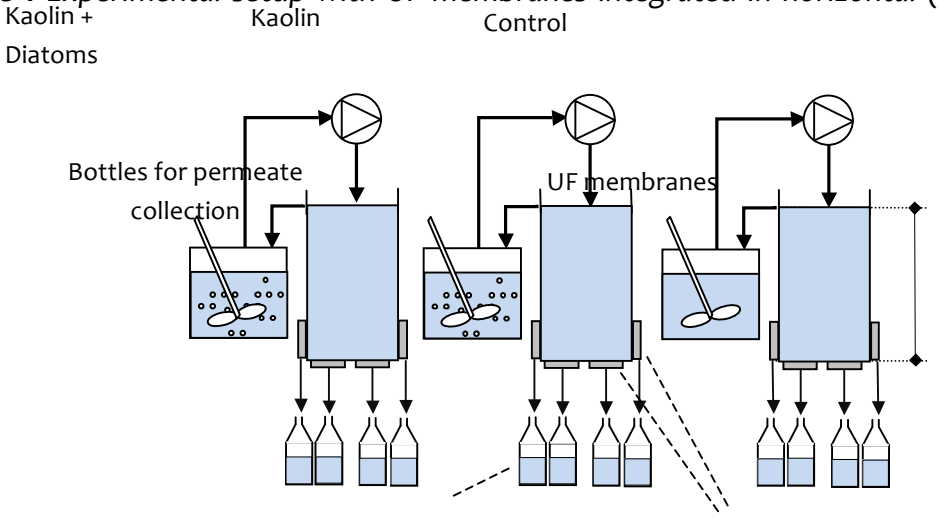


Figure 1 *Experimental setup with UF membranes integrated in horizontal (HOR) or vertical (VER) position.*

Feed water composition

Inorganic particles

Feed waters were modified by adding inorganic particles at a final concentration of 300 mg L^{-1} Kaolin (Fluka, 60609) or kaolin mixed with diatoms (Fluka, 60779) 50/50% by mass. The particle size distribution was determined in triplicate by light scattering measurements (Mastersizer 2000, Malvern Instruments, UK) (Table 1). In addition, the stability of particles against aggregation over time was confirmed by particle size time series measurements. Suspensions of the particles were prepared in pre-filtered (0.22 μm) creek water and their size distribution was measured over a 2-day period. The prepared solutions were stable against aggregation over the 48 hour period, hence the feed water solutions were freshly prepared every second day. Also to verify that the selected particles carry similar charge, their zeta potential was measured in triplicate in deionised water (Zetasizer, Malvern Instruments, UK). Zeta potential of kaolin was -21.8 ± 3.7 mV, while of diatoms -28.7 ± 4.7 mV.

Dissolved and Total Organic Carbon (DOC, TOC)

Pre-filtered (150 kDa membrane, Microdyn Nadir, Germany) creek water was used in experiment A, with by a Total Organic Carbon (TOC) level of 2.7 ± 0.4 mg L^{-1} (SD) and

a Dissolved Organic Carbon (DOC) level of 2.5 ± 0.4 mg L^{-1}. Unfiltered creek water was used in experiment B, with a TOC of 2.5 ± 0.2 mg L^{-1} and a DOC level of 2.1 ± 0.5 mg L^{-1}. TOC and DOC were measured with a total organic carbon analyser (TOC-V, Shimadzu, Japan).

Membrane

Polyethersulfone membranes with a nominal molecular weight cutoff of 100 kDa (Microdyn-Nadir, Wiesbaden, Germany) were used. Prior each experiment each membrane was flushed at least twice with deionised water and then stored 30 minutes in 20% 2-propanol solution to remove conservation agents. Afterwards the membranes were copiously flushed with and stored in deionised water. 24-hour permeability tests were conducted with deionised water to ensure integrity of the membranes and their comparable permeability level (membranes with standard deviation of permeability higher than 10% were discarded).

Resistances to filtration

The resistances of the clean ultrafiltration membrane, biofilms and the clean particle cake were calculated following equation (1) (Katsoufidou et al. 2005):

$$R = {}^{TMP}/_{\eta J} \quad [m^{-1}] \qquad (1)$$

where TMP is a transmembrane pressure [Pa], J is a flux of water expressed as the amount of water V [L] flowing through a defined membrane area A [m^2] in time t [h], and η is dynamic water viscosity [Pa∗s].

The total resistance R_{total} measured during experiments A and B can be expressed as in equation (2):

$$R_{total} = R_{membrane} + R_{biofilm} + R_{irrev.} \quad [m^{-1}] \qquad (2)$$

where $R_{membrane}$ is the clean membrane resistance measured with deionised water over a 24 hour period (clean water flux, CWF); R_{irrev} is the resistance due to irreversible fouling and is expressed by the difference in clean water fluxes measured before and after the experiment. At the end of experiments at least one membrane from each condition was thoroughly flushed with water (to remove all biofilm, $R_{biofilm}$) and clean water flux (CWF) was measured over a 24 hour period. This CWF value was compared with the CWF measured at the beginning of the experiment (clean membrane resistance, $R_{membrane}$) and corresponds to irreversible fouling resistance R_{irrev}.

$R_{biofilm}$ corresponds to resistance due to long term biofilm development and was calculated by subtraction of $R_{membrane}$ and R_{irrev} from the total resistance R_{total} measured in experiments A and B.

In addition, specific biofilm resistance $R_{biofilm, spec}$ [m g^{-1}] was obtained by dividing the biofilm resistance $R_{biofilm}$ with its corresponding total solids TS mass.

In experiment C the hydraulic resistance resulting from the formation of an inorganic particle cake (without biofilm growth) was referred to as R_{cake}. It was defined as the clean particle cake resistance measured with deionised water, for membranes evenly covered with 1 gram of kaolin, or with 1 gram of kaolin/diatoms mix (50/50%). The permeate flux was monitored online (one minute resolution) with balances connected to a PC. The calculated resistance is over a period of at least 30 minutes filtration performed at 20°C, with three membranes used per condition.

Biofilm structure characterisation

Mesoscale level

Optical Coherence Tomography (OCT) (930 nm, Spectral Domain, Thorlabs GmbH, Dachau, Germany) was used to investigate the thickness of the biofilm. The membranes were removed at the end of experiments A and B, placed on a petri dish and imaged immediately. At least five images were taken per each condition. Imaging procedure and analysis were done as described by Derlon et al. (2012).

Microscale level

A Scanning Electron Microscope (SEM; Nova NanoSEM 230 FEG, FEI Inc., Oregon, USA) was operated in low vacuum to image biofilm structure at the microscale. No sample alteration or sputtering was employed, as the instrument allowed for direct observation using a Variable Contrast Detector (VCD). The membranes were removed from the tank at the end of experiment A, attached to the SEM sample holders and immediately taken to the microscope for imaging.

Total and Volatile Solids (TS, VS)

To verify particle accumulation on the membrane surface, volatile and total solids mass were determined at the end of the experiments, following Standard Method (APHA 2005). Accumulated mass was thoroughly removed from the membrane surface (by flushing with deionised water), then filtered with a paper filter. All mass was dried first at 105°C and later burned at 550°C. For experiment A, one membrane

from each condition was analysed. For experiment B, at least two membranes per condition were analysed.

Results and discussion

Effects of particle population on permeate flux

Case of a single population of particles (kaolin)

The changes in the average permeate flux is shown in Figure 2 for the two experiments with pre-filtered and unfiltered feedwater. The influence of the presence of inorganic particles on the filtration performances depended on size of these particles. When the influent contained a single population of fine particles (kaolin, $d_{0.5}$=3.6 µm), low permeate fluxes were observed compared to control and regardless of the membrane arrangement (Fig. 2 c, d). For the horizontal membranes permeate fluxes were reduced to 54% (A) and 68 % (B) of the respective average control flux value (Table S1), and additionally continued to decrease over duration of the experiment due to kaolin accumulation (Fig. 2 c). For the vertical membranes low, but stable permeate fluxes were measured in presence of kaolin. The obtained fluxes were 68% (A) and 45% (B) of the average control flux value (Table S1).

Case of mixed population of inorganic particles (kaolin and diatoms)

While fine particles negatively affected permeation rates, their combination with the larger particles (diatoms, $d_{0.5}$ = 21.9 µm) was able to counterbalance this effect. When the feedwater contained mixed population of the particles, permeation rates depended on the membrane configuration. For the horizontal membranes, stable fluxes similar to control were achieved, despite all particle mass accumulation on the membrane surface (Fig. 2 e). The relative values of 95% (A) and 100% (B) were measured, compared to the average respective controls (Table S1). For the vertical membranes, reduced but stable permeate fluxes were measured 69% (A) and 51% (B), compared to respective average controls (Table S1). These fluxes were similar to the fluxes obtained with kaolin particles in the vertical membrane configuration (Fig. 2 d vs f). In addition, when the system was operated with unfiltered water, the level of flux stabilisation was significantly larger in the horizontal membrane arrangement for the control and kaolin with diatom case, compared to the pre-filtered water experiment (Fig. 2 a, e). Also larger permeate flux variability (seen in

the standard deviation of the flux) for control in the unfiltered creek water, compared to the pre-filtered creek water was observed (Fig. 2 a, b).

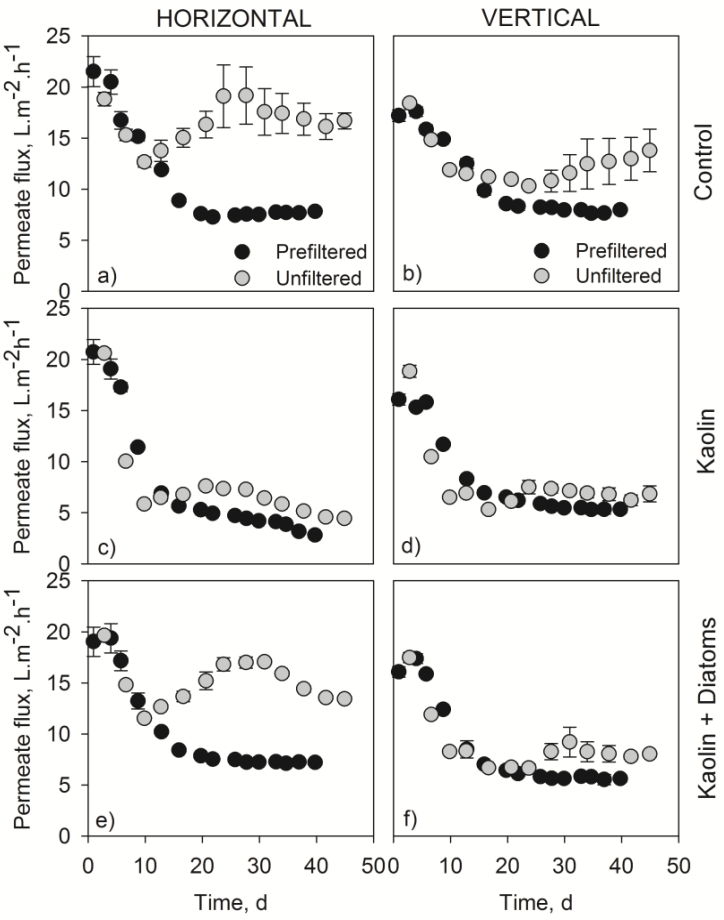


Figure 2 *Permeate flux values obtained during continuous dead-end filtration of creek water, spiked with kaolin or kaolin with diatomaceous earth (50/50%), compared to control (no particle addition), in two membrane configurations: horizontal and vertical. Each error bar indicates standard deviation.*

Biofilm structure and heterogeneity

Biofilm mass was measured at the end of both experiments (Figure 3). The membrane orientation determined how much mass accumulated, with more than 10-fold more total solids in the case of horizontal membranes, compared to the vertical ones (for the condition with added particles).

For the kaolin case in the horizontal membrane arrangement, the accumulated mass was more than 10-times higher than for the respective control (Fig. 3 a, c). The same mass ratio was measured for the kaolin and diatoms case, compared to the controls (Fig. 3 a, e). In summary, the accumulated mass of particles was similar for both kaolin only and kaolin with diatoms, in both membrane arrangements (Fig. 3 c, e; d, f).

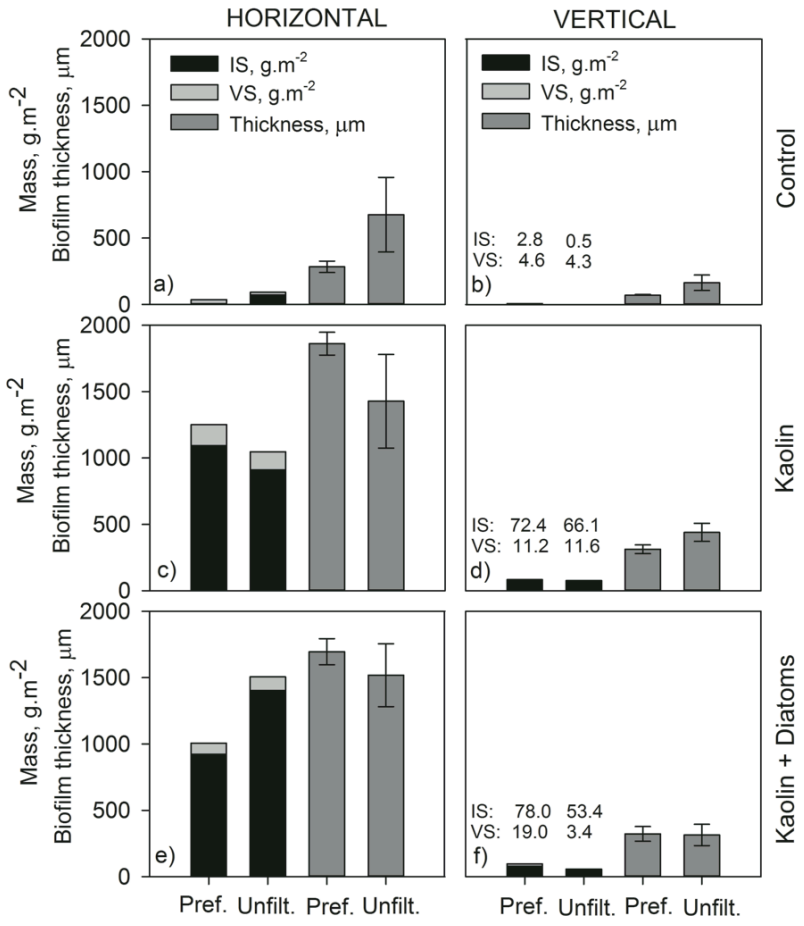


Figure 3 *Comparison of volatile (VS), inorganic (IS) solids and biofilm thickness in two membrane configurations: horizontal and vertical. One membrane filter was weighed at the end of exp. A (prefiltered), two membranes for exp. B (unfiltered creek water). For the vertical configuration numeric values for VS and IS are provided.*

The accumulated mass furthermore correlated with the biofilm thickness (Figure 3), with thickest biofilms formed in the presence of added particles in the horizontal membrane arrangement. The biofilms developed with the inorganic particles were at least 3 times thicker compared to respective controls, in both membrane arrangements (Fig. 3 Hor vs Ver). Furthermore, the biofilm thickness for the kaolin particle case corresponded with the thickness for kaolin and diatoms case, in both respective membrane configurations (Fig. 3 c, e; d, f).

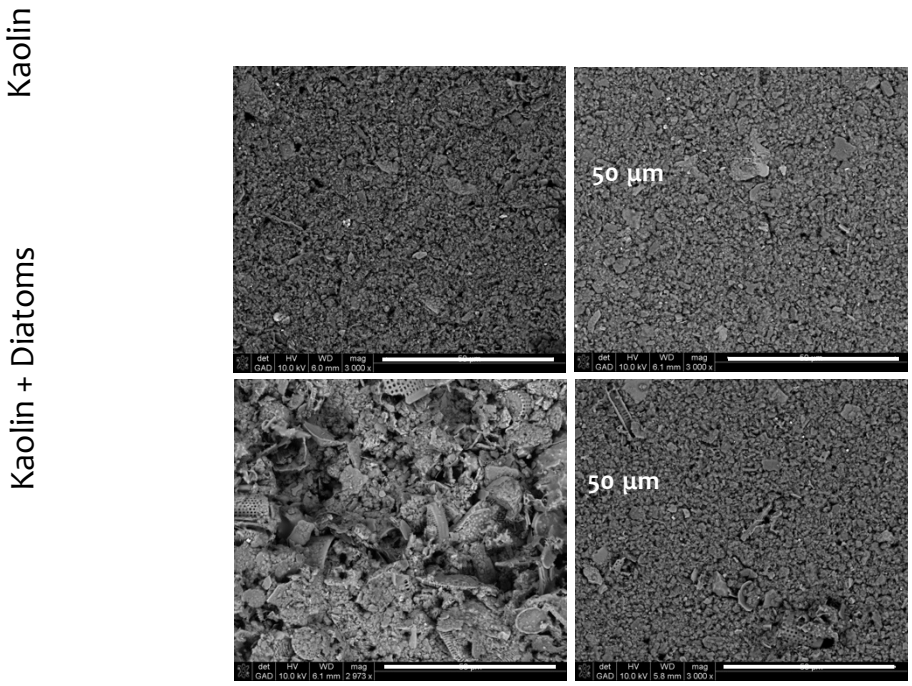


Figure 4 *Scanning Electron Microscopy micrographs of the deposited biofilm layers (in top view) demonstrate effects of particle selection in horizontally (A, C) and vertically (B, D) oriented membranes (experiment A). Membranes were fed with the same raw water, spiked with 300 mg L^{-1} kaolin (A, B) or 300 mg L^{-1} kaolin and diatoms (C, D) (50/50%, by weight). Image size area 100 x 100* µm.

However these mesoscale observations of the biofilm structure (biofilm mass, thickness) were insufficient to explain differences in the filtration performances. Therefore the structure of the biofilms was also characterised at the micro-scale. SEM micrographs taken at the end of experiment A captured the microstructural differences (Figure 4). The microscale biofilm structure depended on the membrane orientation and type of particles present in the influent. The presence of kaolin in the feed water was associated with the formation of homogenous biofilm structures on both horizontal and vertical membranes (seen in Fig. 4 A and B). When the feed water contained both kaolin and diatoms, heterogeneous biofilm structures developed on horizontal membranes (Fig. 4 C), but homogeneous biofilm structures were observed on vertical membranes (Fig. 4 D).

Resistances to filtration

The most resistive biofilms $R_{biofilm}$ developed with fine particle presence (kaolin), in both membrane arrangements (HOR and VER, Table 2). The least resistive biofilms developed under control conditions (no particle presence), in both experiments A and B. However, presence of the diatoms in the horizontal membrane configuration created biofilms of resistance similar to that of control, despite significantly higher biofilm mass and thickness (Table 2 $R_{biofilm}$ HOR).

Overall, resistances of all biofilms were one order magnitude higher than the resistance of the pristine membrane (10^{12} vs 10^{11} m^{-1}, Table 2), except for Control in exp. B, which was the same order of magnitude. Additional clean particle cake measurements (R_{cake} - without biofilm growth) showed that the resistances of the particle cakes were one to two order of magnitudes lower than the $R_{biofilm}$ (10^{12} vs $10^{10\div11}$ m^{-1}, Table 2). Resistance due to irreversible fouling $R_{irrev.}$ (obtained after physical biofilm removal from the membrane surface) was also one order of magnitude lower than $R_{biofilm}$ (10^{11} m^{-1}, Table 2).

Table 2 *Resistances to filtration from experiments A, B and C (standard deviation in parenthesis) for the respective membrane configurations (vertical VER and horizontal HOR).*

			HOR membranes		VER membranes	
Resistances (x 10^{11} m^{-1})		**Deionised water (exp. C)**	**Pre-filtered (exp. A)**	**Unfiltered (exp. B)**	**Pre-filtered (exp. A)**	**Unfiltered (exp. B)**
$R_{membrane}$		For all exp.: 5.1 ± 0.4				
$R_{irreversible}$		For all exp.: 4.7 ± 1.0				
R_{cake}	Kaolin	2.1 ± 2.9	-	-	-	-
	Kaolin+Diatoms	0.6 ± 1.0	-	-	-	-
$R_{biofilm}$	Control		16 ± 1.4	6.5 ± 0.9	14 ± 1.8	12 ± 1.6
	Kaolin		35 ± 8.3	28 ± 7.1	24 ± 3.1	25 ± 3.4
	Kaolin+Diatoms		17 ± 1.4	8 ± 1.3	23 ± 2.4	21 ± 3.0

However analysis of the specific biofilm resistance shown in Fig. 5 (obtained by dividing the biofilm resistance $R_{biofilm}$ with its corresponding total solids mass) shows that the highest specific biofilm resistance developed for the thin biofilms (seen in Control VER; Fig. 5). Accumulation of the inorganic particles during active biofilm growth did not influence the specific biofilm resistance.

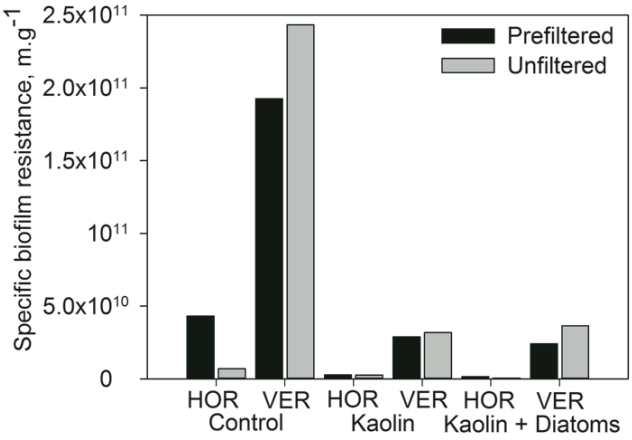


Figure 5 *Specific biofilm resistance from experiment A and B, obtained by division of the biofilm resistance ($R_{biofilm}$) with its corresponding total solids (TS) mass.*

Discussion

How does a particle type influence biofilm structure and flux?

Our results show that the resistance of biofilms was significantly higher than the resistance of the developed inorganic particle cakes ($R_{biofilm}$ vs R_{cake}, Table 2). This indicates that biofouling during GDM filtration is primarily governed by biofilm growth processes (bacterial growth, predation) and not by cake formation. However the specific resistance of biofilms developed in presence of inorganic particles was one order of magnitude smaller than the specific resistance of the control biofilms, without particles (Fig. 5). This suggests that inorganic particles from the feed water influenced the formation of the biofilm physical structure and its permeability.

Heterogeneous biofilm structure with decreased resistance to filtration developed in presence of larger particle fractions, i.e. diatoms (Fig. 4 C). On the other hand homogenous biofilm structure with increased resistance to filtration developed in presence of smaller particles, i.e. kaolin (Fig. 4 A, B, D). Previous investigations of the mesoscale biofilm structure highlighted its influence on the filtration performance (Derlon et al. 2012). Heterogeneous and open biofilm structures helped to maintain high permeate fluxes in low-pressure membrane ultrafiltration. Homogenous and compact biofilm layers indicated low biofilm permeability, and thus lower rates (Derlon et al. (2012), Peter-Varbanets et al. (2011). In our study the biofilm mesoscale measurements showed that biofilms had similar thickness and mass but different hydraulic permeabilities. These mesoscale parameters were not relevant to predict biofilm hydraulic resistances, contrary to the past studies focusing on predation (Derlon et al. 2012). Only microscale observations performed with SEM (Fig. 4) allowed to explain the structural differences of the developed biofilms, which in turn influenced the hydraulic resistance. *Based on volatile solids (VS) measurements (Fig. 3), amount of biomass with the particles was at least 3-4 times higher than biomass in control, indicating that presence of particles enhanced entrapment of the organic matter. However, the detrimental effect on flux was observed only with fine kaolin particles, not with the diatoms. Additionally, biofilm hydraulic permeability depends not only on structure of the biofilm, but also its chemical composition (type of macromolecules, charge). Unfortunately, no investigations were undertaken during this study to identify biofilm chemical composition and interactions with the inorganic particles, such as colloidal destabilization or sorption onto particles, which could have explained the increased*

fouling effects in presence of the colloidal kaolin particles (Jermann et al. 2008a; Jermann et al. 2008b).*

The influence of particulate fractions on formation of different biofilm microscale structure can be explained in three ways. Firstly, the size of the particles determines the packing of the cake and thus its hydraulic resistance. The highest resistances come from the smallest particle fractions, as demonstrated by Kim and Ng (2007) and Carman (1938). In our experiments (kaolin case), kaolin fractions up to 1 µm represented 12% of the overall particle population, while for the diatoms and kaolin mix this value was only 3%. Therefore continuous accumulation of kaolin on the horizontal membranes (Fig. 2 c) led to a progressive flux decline, while on the vertical membranes resulted in low, but stable permeate fluxes. Meanwhile the larger particles (diatoms) did not incur negative effects on flux (compared to control). However, the clean cake resistances which resulted from the accumulation of inorganic particles from the water phase and not the microbial processes (bacterial growth, predation) were one order of magnitude lower than the resistances of biofilms (Table 2). Thus, clean cake resistances cannot explain the observed hydraulic resistances alone.

Secondly, the microbial processes contributed significantly to the total hydraulic resistance in GDM filtration. The biofilm resistance is a sum of the bacterial cells accumulation and exopolymeric substances (EPS) excreted by the biofilm during its growth (Dreszer et al. 2013). In our experiments the presence of microbial activity increased the specific resistance of the particle cake accumulating at the membrane surface. Similar results were reported by Dreszer et al. (2013), where filtration of the bacterial cells resulted in significantly lower biofilm resistances compared to filtration of bacterial cells with active biofilm growth. In our case this is supported by the resistances of the clean particle cakes (R_{cake}), which were a magnitude lower than resistances of the biofilms with the particles ($R_{biofilm}$) (Table 2), and by the specific biofilm resistances (Fig. 5), which were not influenced by the presence of inorganic particles, compared to control (no particles).

Thirdly, homogenous biofilm structures shaped by high amount of small particles may prevent from the positive action of larger microorganisms (i.e. predators) (Derlon et al. 2013). It is indeed visible that experiment B (with all natural microorganisms present) yielded higher fluxes, compared to experiment A (in the absence of grazers, due to feedwater pre-filtration; Fig. 2 Unfiltered vs Prefiltered). This is especially visible for the control (Fig. 2 a Unfilt.) and kaolin with diatoms case (Fig. 2 e Unfilt.) in the horizontal membranes, and confirms that predation in the

feedwater is beneficial to sustain increased permeation rates. Presence of the finer particles (kaolin) (Fig. 2 Unfilt.: c, d, f) counterbalanced the positive effects of predation (Fig. 2 Unfilt. e), resulting in lower permeation rates. The membrane orientation (HOR vs VER) played a role in not only pre-sedimentation of the inorganic particles, but also higher microorganisms – the fluxes were lower in the vertically oriented membranes, compared to the horizontal ones (Fig. 2 Unfilt.).

It is probable that chemical interactions occurred between particles and the biofilm itself or accumulating organic foulants, which lead to increased filtration resistances (Jermann et al. 2008a, Jermann et al. 2008b). Moreover behaviour of particles in deionised water and in creek water could be significantly different due to lack of ions in the deionised water. Typically, in presence of high ionic strength the fouling is more severe, due to electrostatic interactions between the particles (Bowen and Jenner 1995, Faibish et al. 1998).*

Relevance for small scale water treatment systems

In our study the vertical or horizontal membrane configuration determined which particles accumulated on the membrane surface during long-term gravity driven membrane filtration. The selective accumulation of small particles on vertical membrane surface (due to settling out of the larger particles) brought additive resistance to the growing biofilm. On the contrary, larger particles accumulating on horizontal membrane surface counterbalanced this negative effect, resulting in higher filtration performances. Therefore pre-selection of particles (as well as higher microorganisms) was detrimental to permeation rates in the GDM system. Filtration with accumulation of the larger particles in the horizontal membrane mode allowed for continuous filtration at flux values comparable to the control, without the use of cross-flow. Thus the approach proved relevant for long term filtration without the need for electricity (to remove accumulating particles) or membrane cleaning.

Gravity driven membrane ultrafiltration, operated without electrical energy requirements is a relevant solution for small scale water treatment systems. Currently the GDM systems are installed in developing countries (Boulestreau et al. 2012, Hoa and Lesjean 2009), where they are used for surface water filtration (pond, lake, river). These waters vary in particulate fractions size and content. Taking in account that removal of all particles is unfeasible (additional pre-treatment installation, additional cost), pre-filtration of the feedwaters should be avoided. Such pre-filtration not only selects most resistive particle fractions, but

also removes natural microbial communities (such as grazers), which enhance permeation rates in GDM ultrafiltration. The limitation of continuous particle accumulation is that with time even the larger particles may impose an increased resistance to filtration - and no further flux gain will be observed. In this case the membranes should be gently flushed to remove all accumulated mass.

Conclusions

Biofouling during GDM filtration resulted from (i) microbial processes such as bacterial growth and (ii) cake formation due to accumulation of particles from the water phase. The microbial processes contributed the most to the hydraulic resistance. However the type of inorganic particles also influenced the total resistance to filtration. Presence of larger inorganic particles increased the biofilm micro-scale heterogeneity. This counterbalanced the negative effects of fine particle accumulation, leading to development of a heterogeneous biofilm structure with lower resistance to filtration.

Selection of the inorganic particles (due to their pre-sedimentation in the vertical membrane arrangement) promoted fine homogenous particles accumulation which offered increased hydraulic resistance in the biologically active membrane filtration. In case of turbid raw waters, such pre-sedimentation may actually reduce the permeation rates due to removal of large, heterogeneous particles.

Therefore in case of feed waters containing high concentration of particles, both membrane orientation and type of the particles will play a role in determining the biofilm permeability. When fine particles dominate in the raw water, it is better to operate the membranes in the vertical arrangement, minimising the particle accumulation. When larger particle fractions are present, it is favourable to operate the membrane in the horizontal arrangement, allowing for the particle sedimentation.

For practical optimisation of low-pressure ultrafiltration, particle pre-treatment of raw waters later treated in the low pressure ultrafiltration systems selects finest particles and may lead to a significantly increased resistance to filtration.

Abbreviations

ATP	Adenosine Triphosphate
CWF	Clean Water Flux
DOC	Dissolved Organic Carbon
EPS	Exopolymeric Substances
FEG	Field Emission Gun
GDM	Gravity Driven Membrane
HOR	Horizontal
kDa	kilo Dalton
OCT	Optical Coherence Tomography
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SD	Standard Deviation
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
TS	Total Solids
UF	Ultrafiltration
VER	Vertical
VS	Volatile Solids

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SUPPLEMENTARY INFORMATION

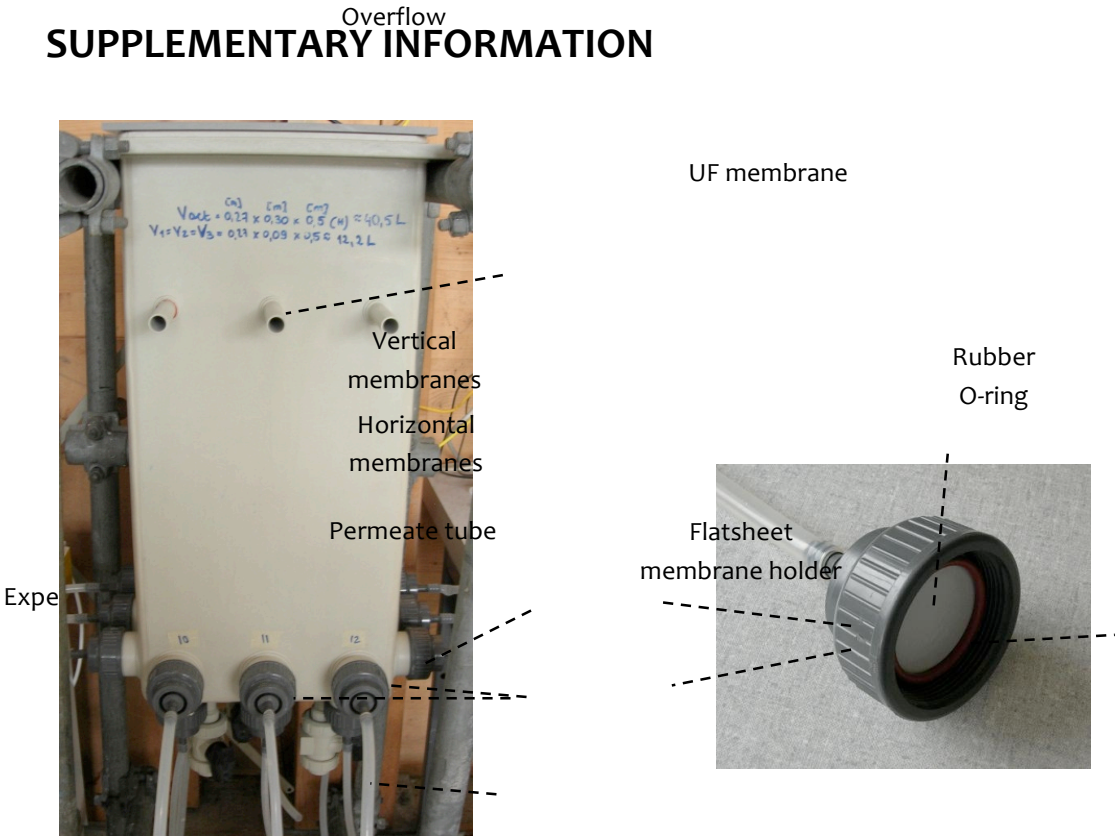

Figure S1 *Photograph of the experimental tank and the flatsheet membrane holder.*

Table S1 *Permeate fluxes from experiments A and B with standard deviation, for the respective membrane configurations (vertical VER and horizontal HOR). The average flux values were calculated over the stabilised flux period. The % of flux is referred to the control average value.*

	HOR membranes				VER membranes			
Permeate flux ($Lm^{-2}h^{-1}$)	**Pre-filtered (exp. A)**	%	**Unfiltered (exp. B)**	%	**Pre-filtered (exp. A)**	%	**Unfiltered (exp. B)**	%
Control	7.6 ± 0.2	-	17.1 ± 1.4	-	8.1 ± 0.3	-	11.9 ± 1.2	-
Kaolin	4.2 ± 0.8	54	6.2 ± 1.2	41	5.3 ± 0.4	68	6.7 ± 0.7	45
Kaolin + Diatomite	7.4 ± 0.2	95	15.2 ± 1.5	100	5.4 ± 0.3	69	7.7 ± 0.9	51
Control Average (HOR + VER)			exp. A: 7.8 (0.1)		exp. B: 15.0 (0.8)			

Table S2 *Total ATP (adenosine triphosphate) measured at the end of experiment A (with pre-filtered water) from the accumulated biofilm, expressed per m^2 of membrane.*

	Total ATP, RLU m^{-2} membrane	
	HOR	**VER**
Control	6.2×10^{10}	9.6×10^{10}
Kaolin	5.1×10^{10}	2.9×10^{10}
Kaolin + Diatomite	12×10^{10}	3.7×10^{10}

Chapter 4

Biofilm increases permeate quality by organic carbon degradation in low pressure ultrafiltration

This chapter has been submitted as:

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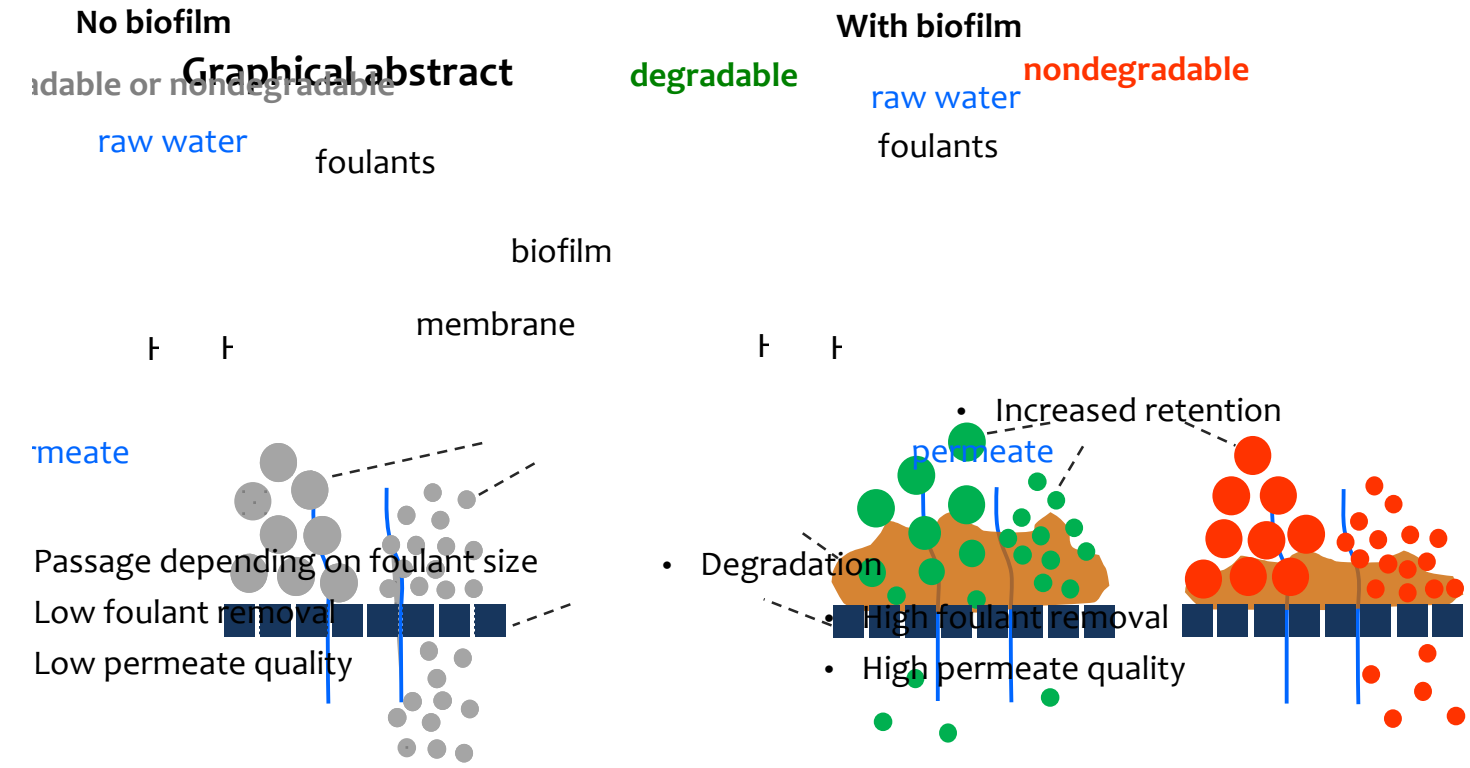
No biofilm
Graphical abstract
degradable
With biofilm
nondegradable
raw water
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biofilm
membrane
permeate
Passage depending on foulant size
Low foulant removal
Low permeate quality
Degradation
Increased retention
permeate
High foulant removal
High permeate quality

Abstract

We investigated the influence of biofouling of ultrafiltration membranes on the removal of organic model foulants and ultimately on the quality of permeate. Gravity driven membrane ultrafiltration (GDM) membrane systems were operated with modified creek water during five weeks without control of the biofilm formation. Three GDM systems were studied: two systems with biofilms exposed to (A) variable or (B) constant load of organic foulants, and (C) one system without biofilm exposed to constant foulant loading. Biodegradable dextran or nondegradable polystyrene sulfonate model foulants were tested, with substrate degradability confirmed by Size Exclusion Chromatography (SEC) and in a degradation batch (D). The GDM systems (A) and (B) were fed with pre-filtered creek water supplemented with dextran (Dex) 1, 150 or 2000 kDa, or polystyrene sulfonate (PSS) 1 kDa or 80 kDa at a concentration of 2 - 3.5 mgC L^{-1}. In exp. (C) the feed was deionised water with 25 mgC L^{-1} of either PSS 1, 80 kDa, or Dex 2000 kDa.

The biofilm formation on UF membrane surfaces controlled the foulant permeation and thus the permeate quality. Biofilms exposed to continuous foulant loading (exp. B) directly utilized low molecular weight (LMW) biodegradable foulants (1 kDa Dex) as substrate, which improved the permeate quality. For high molecular weight (HMW) substrates (150, 2000 kDa Dex) the permeate quality improvement was observed after 7 days of biofilm formation, due to initial foulant hydrolysis followed by degradation. For nondegradable substrates, 20% improvement in the retention was observed for the polystyrene (1, 80 kDa PSS) due to physical presence of the biofilm, compared to the virgin membrane retention. For variable foulant loading (exp. A) the biofilms did not uptake the substrate directly, which resulted in their hydrolysis and ultimately permeate quality decline, except for the LMW dextran (1 kDa). The retention of HMW dextrans (150, 2000 kDa) declined due to their hydrolysis to smaller fractions that were permeating through the membrane. Thus continuous biofilm exposure to the foulants resulted in increased foulant removal, with biofilms more efficient in foulant removal than the virgin membrane retention and more efficient than biofilms which were exposed to the foulants on an intermittent basis.

The foulant retention and degradation also influenced permeate fluxes. In presence of the biofilm, the highest fluxes were observed for control (no foulant) and nondegradable and non-accumulating foulant PSS 1 kDa. Low fluxes were observed for the accumulating on membrane surface or degradable foulants (exp. B). However, the lowest fluxes were observed in absence of the biofilm (exp. C), due

to physical accumulation of the foulants (PSS 80 kDa and Dextran 2000 kDa). The biofilm presence protected the membrane from further fouling and the permeate flux stabilized with the biofilm-membrane composite, compared to the membrane only.

Keywords

biofilm, foulant, Gravity Driven Membrane (low pressure) ultrafiltration, permeate quality, substrate degradation

Introduction

In conventional large-scale membrane filtration systems the formation of biofilms on membrane surfaces increases the hydraulic resistance, which reduces the permeate flux. For this reason the presence of biofilms of membrane surfaces is considered to be detrimental for the process operation. Periodic physical and chemical cleanings are performed to limit biofilm growth and maintain high permeate fluxes (Flemming et al. 1997). Another approach is feed water pre-treatment to remove nutrient load and limit biofilm growth potential (e.g. by biofiltration, Huang et al. (2009), Huck et al. (2011), Peldszus et al. (2012)). While these control strategies help to reduce the detrimental effect of biofouling on permeate flux, practical experience shows that the formation of biofilm in membrane systems cannot be eliminated entirely.

On the other hand, recent studies reported that biofouling might not always be detrimental as it can also enhance permeate quality. Biofouling can increase the retention of different compounds that can permeate through clean membranes, e.g. assimilable organic carbon (Derlon et al. 2014), specific microbial toxins (Kohler et al. 2014), viruses (Lu et al. 2013), antibiotics (Shen et al. 2014) polymeric organic substances (Kang et al. 2007). However, most studies were based on membrane bioreactor systems with high biomass concentrations (Kang et al. 2007, Shen et al. 2014), or on short-term filtration experiments (Lu et al. 2013) with biofouling strongly limited using intensive control strategies.

Gravity-driven ultrafiltration is a special case of membrane filtration, where formation of biofilm on membrane surface is tolerated. The biofilm allows for long-term operation of the membrane system at a stable permeate flux (Peter-Varbanets et al. 2010). Tolerating biofilm formation in GDM also helped to remove assimilable organic carbon (Derlon et al. 2014) and almost 100% of microbial toxins (microcystins) that were permeating through virgin membranes (Kohler et al. 2014). Derlon et al. (2014) and Peter-Varbanets et al. (2011) further showed high organic biopolymer removal during long term river water filtration with the biofilm present on the membrane surface. But the exact mechanisms responsible for the biopolymer removal, e.g. degradation or physical retention, were not identified. Due to the dead-end filtration mode, all foulants present in the feed water either permeate through or accumulate on the membrane surface. Thus, the biofilm present on the ultrafiltration membrane surface is continuously exposed to these foulants. When feedwaters contain biodegradable foulants, it can be hypothesized that the biofilms could be beneficial due to degradation capability of these foulants.

The biofilm might also act as a physical barrier that increases physical foulant retention, such as increased antibiotic retention (Shen et al. 2014). On the other hand, negative effects of biofilm presence could be hydrolysis of foulants to smaller size fractions that would permeate through the membrane and become source for bacterial regrowth (Derlon et al. 2014). Both degradation of biodegradable and accumulation of nondegradable foulants could furthermore affect permeate flux due to additional accumulation and biofilm growth. The contribution of biofilm presence onto degradation and retention of foulants, as well as permeate flux during long term GDM ultrafiltration is unclear and therefore understanding is required.

The objectives of this study were therefore: (1) to evaluate how presence of biofilm influences retention of biodegradable and nondegradable foulants (2) to determine how the foulant influences the formation of the biofilm and in turn the permeate flux, and (3) to determine if biofilms can represent an additional efficient barrier that prevents further membrane fouling due to foulant accumulation. Gravity-driven ultrafiltration membranes with/without biofilms were operated in dead end-mode (no cross-flow) and fed with biodegradable or nondegradable organic foulants. Dextrans (1, 150 and 2000 kDa) or polystyrene sulfonate PSS (1, 80 kDa) were used as model foulant. Dextrans represented biodegradable substrates, while PSS represented the nondegradable ones. Biofilms on membrane surfaces were exposed to constant or variable foulant loading over several weeks. The constant or variable foulant loading experiments aim to differentiate when the biofilm removes the foulants most efficiently (filtration conditions, type of foulant).

Material and methods

Experimental conditions and setup

Four different experiments were performed (Table 1). Experiments A and B aimed at evaluating how biofilm formation on membrane surfaces influences removal of foulants and ultimately foulant concentration in permeate. The biofilms were exposed to variable foulant load (exp. A) or constant foulant load (exp. B). In exp. A the foulants were added intermittently, for 24 hrs at weekly intervals, while in exp. B the foulants were fed continuously. Experiment C aimed at evaluating the effect of constant foulant load on the permeate flux in the absence of biofilm. A short batch (exp. D) was conducted to assess the biodegradability of the different model foulants.

Experiments A and B were conducted using identical setups (Fig. 1). The feed water was distributed from the storage tank to each biofouling monitor. An overflow was used to keep the water level at a constant 70 cm, corresponding to transmembrane pressure of 70 mBar. Six parallel experimental lines were installed in both experiments - one control (no addition) and five lines with foulant addition (dextran 1, 150 or 2000 kDa, PSS 1 or 80 kDa). Two biofouling monitors (equal membrane area: 0.00191 m^2) were installed at each line. No foulant was added in the control line, while one foulant type was dosed into each of the other five lines. The foulant solution was daily prepared in a sterile glass bottle and then fed to the biofouling monitor with a fine dosing pump (Ismatec IPC ISM932D, IDEX). All experiments were performed at 20°C, with permeate collected in bottles and weighed regularly. In Exp. C the same setup was used (Fig. 1), but the biofouling monitors, tubing and glassware were autoclaved in order to minimise biological activity and biofilm development on the membrane surface. Experiment D was conducted in six identical 2 L glass bottles, constantly mixed.

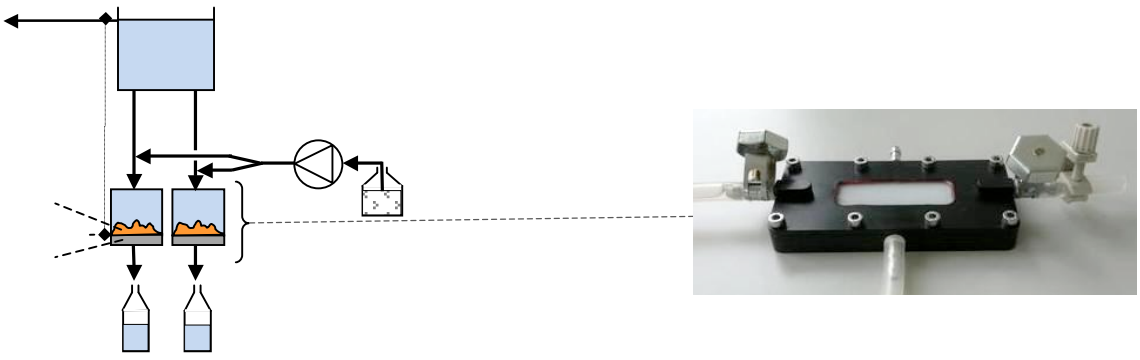

Figure 1 *Experimental setup with addition point of the foulants - dextrans or polystyrene sulfonates (left), and the biofouling monitor (right). Each experimental line consisted of two biofouling monitors fed from a daily prepared, autoclaved creek water solution. No foulant was added to control. Six identical experimental lines were used in parallel for both experiments A and B.*

Table 1 *Summary of the experimental conditions with the foulant addition: variable load foulant addition (one day per week, exp. A), constant load foulant addition (exp. B), short term foulant addition in absence of biofilm (exp. C) and foulant degradation batch test (exp. D). The control in (A) and (B) is creek water prefiltered and diluted by 50% with deionised water, in (C) is deionised water DI, and in (D) it is creek water.*

Experiment	Duration	Condition	Foulant molecular weight, kDa	Foulant concentration, mgC L^{-1}	Expected results
(A) variable load (intermittent addition)	Long term (4.5 weeks)	• Control • Dextran • PSS	• - • 1, 150, 2000 • 1, 80	• - • 2 • 2	Decreased foulant removal due to hydrolysis
(B) constant load (continuous addition)	Long term (5 weeks)	• Control • Dextran • PSS	• - • 1, 150, 2000 • 1, 80	• - • 3.5 • 3.5	Increased foulant removal due to hydrolysis and uptake
(C) flux decline without biofilm	Short term (14 days)	• Control (DI) • Dextran • PSS	• - • 2000 • 1, 80	• - • 25 • 25	Flux decline due to accumulation of large molecular weight foulants (no biofilm)
(D) batch degradation	Short term (4 days)	• Control • Dextran • PSS	• - • 1, 150, 2000 • 1, 80	• - • 2.5 • 2.5	Degradation of dextrans and non-degradation of polystyrene sulfonate

Feed water composition

Model foulants

Feed waters were prepared with different model foulants: dextran of molecular weights of 1, 150 or 2000 kDa (CAS 9004-54-0, Sigma Aldrich, Switzerland) or polystyrene sulfonate (PSS) sodium salt (CAS 9080-79-9, Polymers Standard Service, Germany) of 1 or 80 kDa at a final concentration of 2 or 3.5 mgC L^{-1} (25 mgC L^{-1} for exp. C). All dextrans and PSS polymers were GPC grade. Size Exclusion Chromatography (SEC) (DOC-Labor Drs. Huber, Germany) confirmed their molecular weight distributions.

Feed water preparation

The feed waters for exp. A were prepared in sterile glass bottles using deionised water (concentration of 2 mgC L^{-1} as organic carbon). In exp. B the feed waters were prepared in sterile glass bottles at a concentration of 3.5 mgC L^{-1} as organic carbon. The bottles were filled with 1L pre-filtered (0.45 µm) creek water diluted by 50% with DI water and were autoclaved for 4 hours. The different model foulants were then added freshly to the autoclaved feed water. For exp. A and B, each bottle was prepared and replaced on a daily basis. For exp. C (no biofilm growth), all glassware and tubing were autoclaved prior to the experiment to eliminate microbial activity. The foulants were prepared in autoclaved deionised water under

laminar flow bench (concentration of 25 mgC L^{-1} as organic carbon). The feed waters were prepared fresh and replaced on a daily basis. In addition, a short degradation batch experiment was conducted to confirm the degradability of the studied foulants (Table 1, experiment D). The foulants were added on day 1 into completely mixed glass reactors (thermostated at 20°C), filled with 1 litre of prefiltered creek water. The initial concentration of foulants was 2.5 mgC L^{-1} and was monitored daily (Fig. S1).

Size exclusion chromatography (SEC) and total organic carbon (TOC)

All feed water and permeate samples for the chemical analyses were taken fresh and directly at the source. The samples were collected into analysis vials (4h at 450°C) and analyzed immediately. TOC was measured on at least 5 (Exp. A) and 6 (Exp. B) different days, after complete organic carbon oxidation in a Graentzel thin-film reactor (DOC-Labor Dr. Huber, Germany). Additionally, samples were characterized by size exclusion chromatography (SEC) coupled to an organic carbon detector. Size exclusion column Toyopearl TSK HW-50S with a fractionation range of 100 – 20,000 Da was used. Organic carbon was detected by an infrared detector (DOC-Labor Dr. Huber, Germany). The chromatography results were analyzed with the instrument software (Huber and Frimmel 1996). A phosphate buffer was used as the eluent (24 mM, pH 6.6) and the flow rate was set at 1 mL min^{-1}. The detection limit was 10 µg C L^{-1}.

Membrane

Polyethersulfone membranes with a nominal molecular weight cutoff of 10 kDa (Microdyn-Nadir, Wiesbaden, Germany) were used. Prior each experiment, each membrane coupon was flushed at least twice with deionised water and then stored 30 minutes in 20% 2-propanol solution to remove conservation agents. Afterwards the membranes were copiously flushed and stored in deionised water. 24-hour permeability tests were conducted with deionised water to ensure integrity of the membranes and their comparable permeability level. Membrane coupons with standard deviations of permeability higher than 10% were discarded.

Foulant retention tests

The retention of foulants by the ultrafiltration membrane was calculated based on TOC measurements using Eq. 1.

$$R_{TOC} = \frac{C_{creekwater,in} + C_{foulant,in} - C_{creekwater,out} - C_{foulant,out}}{C_{creekwater,in} + C_{foulant,in}} \cdot 100 \ [\%] \qquad (1)$$

where $C_{creekwater,in}$ and $C_{creekwater,out}$ represent the dissolved non biodegradable organic carbon concentrations in the influent and permeate, respectively. $C_{creekwater,in}$ and $C_{creekwater,out}$ were determined from the "control" (no foulant addition), and both had basically the same organic carbon concentrations. $C_{foulant,in}$ and $C_{foulant,out}$ is the organic carbon concentration of the model foulants in the influent and permeate, respectively. The foulant concentration in the permeate water was calculated by subtracting TOC_{in} (which was a sum of $TOC_{creekwater,in}$ + $TOC_{foulant,in}$) minus $TOC_{creekwater,out}$, since $TOC_{creekwater,in}$ equalled to $TOC_{creekwater,out}$ due to non-degradability of creek water TOC. The foulant retention tests were determined for three conditions: (1) *clean membrane* (prior to experiment) measured over a 72 hour period; (2) *with biofilm growth* (during the experiments); (3) *after the biofilm removal* from the membrane surface (at the end of experiments, Fig. 2). For the measurement of the foulant retention by the virgin membranes, the substrates were dissolved in deionised water and concentrations measured daily over a 3 day period. For (2), concentrations were measured on selected days during the main experiments A and B. For (3), the biofilm was thoroughly removed by physical flushing from the membrane surface, the foulants were dissolved in deionised water and permeated through the membrane over a 24 hour period.

Biofilm characterisation

Total and volatile solids (TS, VS)

The biofilm mass accumulated on the membrane surfaces was measured as volatile and total solids mass at the end of the experiment B (constant foulant loading) following Standard Method (APHA 2005). All accumulated biomass was thoroughly removed from the membrane surface (by flushing with deionised water), then filtered with a 0.4 μm paper filter. Biofilm samples were then dried at 105°C and later burned at 550°C. All solids were volatilized at 550°C, meaning no inert mass accumulation took place. One membrane from each condition was analysed and the results are in Table 2.

Biofilm protein content

Biofilm extracellular polymeric substances (EPS) were extracted at the end of experiment B (constant foulant loading) and the protein mass was measured. The protein content was compared with TS measurements to help differentiate between foulant accumulation and biofilm growth for nondegradable foulants. One biofouling monitor from each experimental condition was analysed. The protein

content of biofilms was measured using Sigma Aldrich QuantiPro BCA assay kit (range 0.5-30 mg protein L^{-1}) with 1 to 1 ratio staining (400 µl of sample + 400 µl of reagent). The biofilm was mechanically removed (by flushing) into 45 mls PBS buffer, in which it was sonicated. Each sample (collected in carbon free glass flasks) was placed within crushed ice to keep it cool during sonication. The sonication was done with 0.75 Watt ml^{-1} power density (point sonicator Bandelin Sonoplus HD3200, Germany) with steps as follow: 2 min sonication, followed by 1 minute interval and 2 minute sonication. After the first sonication step, all samples were centrifuged at 5000 G for 20 minutes. The supernatant was used for first protein staining (extraction 1), while the biofilm sludge that accumulated after centrifugation was re-suspended in 45 ml PBS buffer and once again sonicated and centrifuged (as described above). The supernatant from the second step was used for second protein staining (extraction 2). The sum of both extractions (1+2) provided the final amount of proteins.

Results

Effects of foulant molecular weight on permeate quality

Case 1: variable foulant loading

The change in the retention of different model foulants due to the presence/absence of biofilms on membrane surfaces is shown in Fig. 2a for the case "variable foulant loading". The molecular weight (MW) of the model foulants determined their retention by virgin membranes (Fig. 2a, VM). For example, the retention of dextran by virgin membranes increased from 0 to 75% when the MW of dextran increased from 1 to 2000 kDa, which is in agreement with a common cut-off curve of an UF membrane. On the other hand, presence of biofilms on the membrane surface helped to increase the retention of foulants. In presence of biofilms the foulant retention depended on the foulant biodegradability as well as on the molecular weight (MW). The retention of low MW dextran (1 kDa) progressively increased to almost 100 % after few days of biofilm formation. Contrarily, a steep decrease in the retention of high MW dextrans was observed (150, 2000 kDa Dex) during the first days of filtration (Fig. 2a). After 1st week of filtration the retention of high MW dextrans improved steadily but remained around 30% below the virgin UF membrane retention. For the nondegradable foulants, the presence of biofilm slightly improved the retention of both low MW and high MW foulants (10-15%). This could be due to penetration of EPS into membrane pores, reducing their effective diameter.

The change in permeate quality that resulted from the foulant removal was evaluated by SEC-OCD (Fig. 3 a, e). The peaks corresponding to the biodegradable foulants (dextran) became smaller and shifted to the right. This means shorter retention time and ultimately smaller foulant size than in feedwater. For dextran 1 kDa, full degradation of the foulant was observed after 3 days. This is indicated by similar chromatograms for the feed water and the permeate. For high MW dextran around 10 days of biofilm formation were required to observe a significant degradation (Dex 150 and 2000 kDa). For the nondegradable foulant PSS 1 kDa, the chromatograms of the permeate remained similar to the one of the feed water (Fig. 3 a, e). The chromatograms recorded for the nondegradable foulant PSS 80 kDa confirmed the full retention of this foulant by the membrane (Fig. 3 a-e).

Case 2: constant foulant loading

Under "constant foulant loading" conditions the presence of biofilm on membrane surface significantly increased the retention of model foulants, compared to the virgin membrane retention (Fig. 2 b). At constant foulant loading, the retention of foulants was higher than those observed for "variable foulant loading" condition (Fig. 2 b vs a). In this case, the foulant retention by the biofilm-membrane composite was influenced the foulant biodegradability, and not by the MW of the foulant. For all biodegradable foulants, a very high retention and ultimately a significant improvement in the permeate quality was observed due to the presence of biofilm. For 1 kDa Dex, the retention reached more than 90% after 3 day of biofilm formation and then stabilised at almost 100% after 7 days. For both 150 and 2000 kDa dextrans, the retention improved significantly after 7 days of biofilm formation and also reached around 100%. Such retention efficiencies achieved by the biofilm-membrane composites were much higher than the ones observed for virgin membrane (-16, 56 and 80 % for 1, 150 and 2000 kDa dextran, respectively). For nondegradable substrates (PSS), the retention increased with the development of the biofilm, from 0% to 20-30% for PSS 1 kDa and from 60% to almost 100% for PSS 80 kDa.

The mechanisms involved in the removal of model foulants by biofilm-membrane composites exposed to constant foulant loading were investigated (Fig. 3 a-d). Clear changes in the chromatograms of permeate were observed for the biodegradable foulants. The dextran peaks became smaller and shifted to the right after 1 and 3 days of biofilm formation (Fig. 3 b-c) and completely disappeared after 7 days of biofilm development (Fig. 3 d). The peak corresponding to the nondegradable foulant PSS 1 kDa in permeate (Fig. 3 b-d) remained in similar shape

and retention time as in feedwater (Fig. 3 a), while the peak of nondegradable foulant PSS 80 kDa disappeared in permeate (Fig. 3 b-d) due to retention by the membrane.

Case 3: without biofilm

Virgin membrane retention (VM) as well as foulant retention after physical biofilm removal (flush-off) are shown in Fig. 2. The virgin membrane retention for dextrans was: 1 kDa: - 16%, 150 kDa: 55%, 2000 kDa: 82%, and for PSS was: 1 kDa - 2%, 80 kDa: 65%. When the biofilms were removed from the membrane surface after the experiments, the foulant retention was in the range of the VM retention level. Only slight retention changes were observed for Dex 1 kDa – the retention increased to 2% (from - 16%), Dex 2000 kDa – retention decreased to 70% (from 82%), and PSS 80 kDa increased slightly to 78% (from 65%). The negative retentions for 1 kDa dextran could be explained by low TOC concentrations in control feedwater (less than 1 mg mgC L^{-1}), with natural organic molecules undergoing conformational changes due to i.e. decay, which affected their retention.

Biofilm composition

Biofilm mass and protein content were measured at the end of experiment B (Table 2). The foulant degradability and MW determined how much biofilm accumulated during the experiment. The addition of biodegradable foulant increased the mass of biofilms grown on the membrane surface. For dextrans, the biofilm mass was at least 10 fold higher than the control, irrespective of the dextran MW. For nondegradable PSS, the biofilm mass was 3 fold higher for 1 kDa PSS, and 10 fold higher for 80 kDa PSS (due to its accumulation), compared to control. The biofilm protein (EPS) content depended mainly on degradability of the foulant. Highest protein concentrations were measured for the biofilms developed in presence of biodegradable foulants, i.e. dextrans (almost 2 fold higher as in control). For the nondegradable PSS, the protein level was similar to control for 1 kDa PSS, and half the control content for 80 kDa PSS (possible inhibitory effects due to PSS accumulation).

a

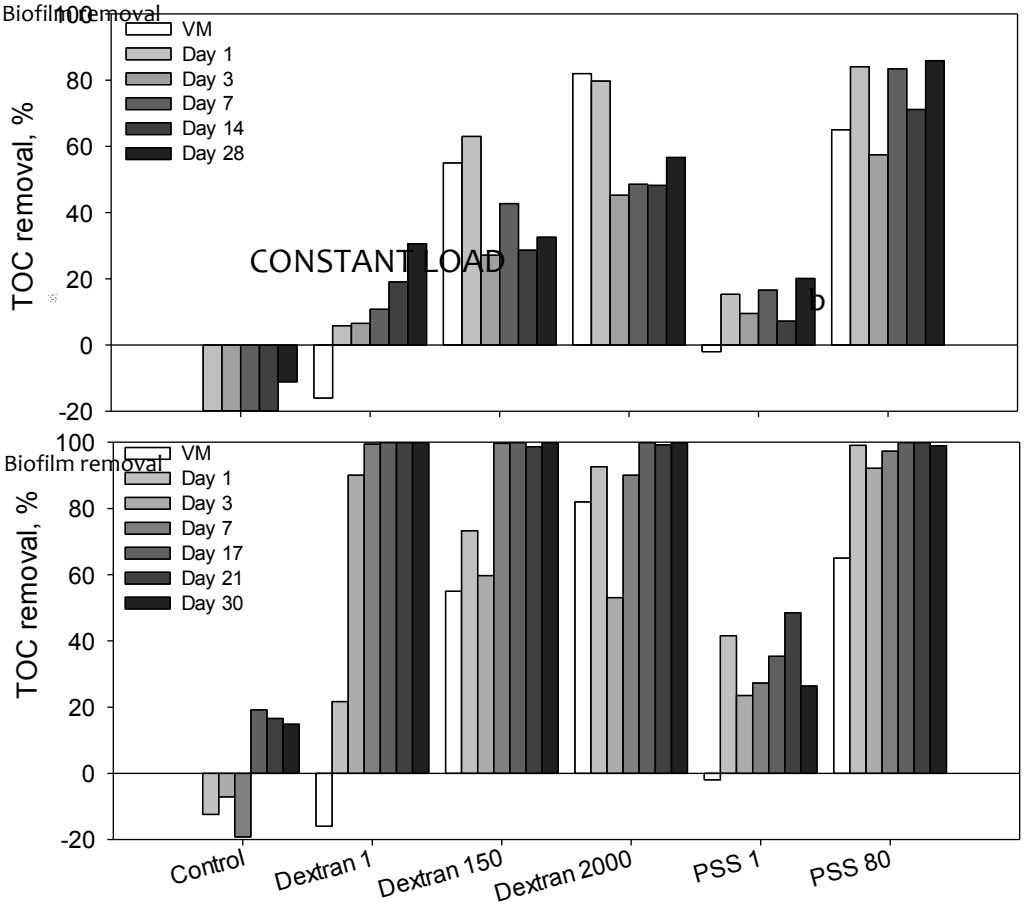

Figure 2 *Permeate quality for Exp. A and B, based on retention and degradation of foulants (TOC measurements). Each error bar indicates a standard deviation. a – variable load experiment, b – constant load. The retentions are compared to the virgin membrane retention (VM) and retention after the biofilm was removed from the membrane surface, at the end of experiment (indicated by the dashed line – – – –).*

Table 2 *Biofilm mass (TS) and protein determined at the end of experiment B (continuous foulant addition), per membrane area. One sample was analysed per condition.*

Condition	TS, g m^{2-}	EPS, g prot m^{2-}
Control	0.48	0.48
Dextran 1 kDa	4.76	0.94
Dextran 150 kDa	7.48	0.88
Dextran 2000 kDa	4.95	0.90
PSS 1 kDa	1.52	0.54
PSS 80 kDa	5.05	0.23

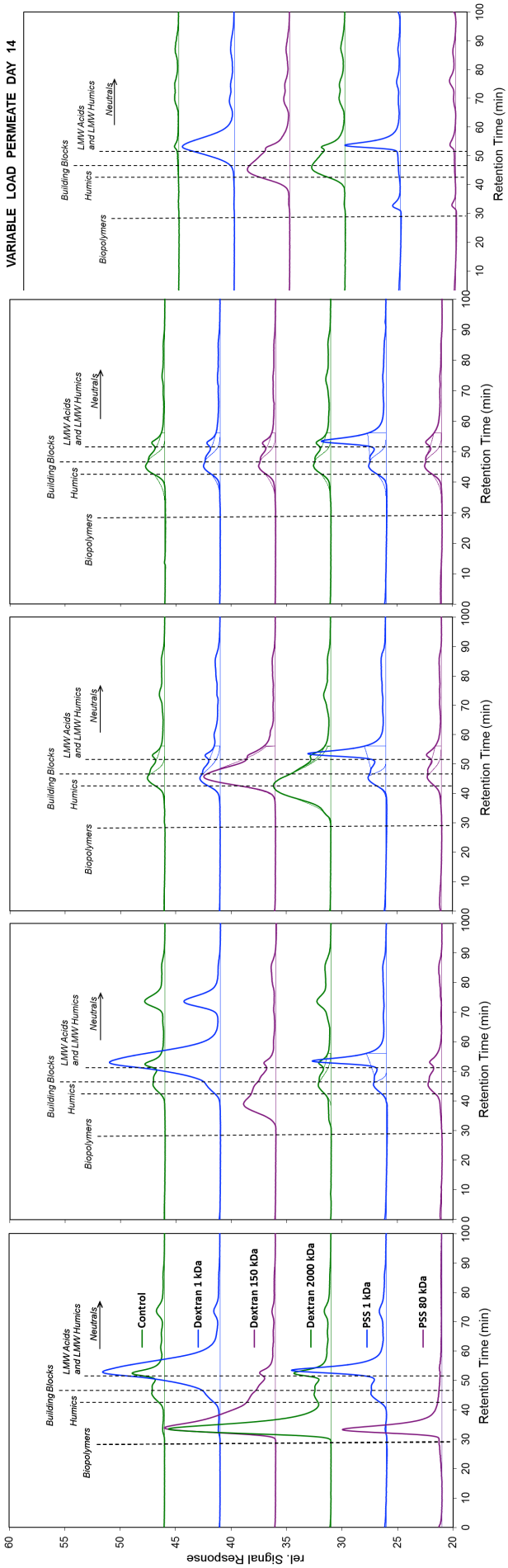

Figure 3 *Feedwater (a) and permeate (b-e) quality for the constant and variable foulant load case, on different days of filtration, based on size exclusion chromatography. The biofilm hydrolysed large molecular weight degradable foulants (dextran 150 and 2000 kDa) into smaller fractions, which permeated through the 10 kDa ultrafiltration membrane. Nondegradable foulants PSS 1 and 80 kDa were not degraded.*

Permeate flux

Permeate fluxes were measured during experiments A, B and C (Fig. 4). The intermittent foulant addition (exp. A) did not influence the permeate fluxes. Permeate fluxes measured with intermittent addition of foulants were similar to the control (no foulants) for exp. A. The amount of added foulants was insufficient for significant biofilm growth or foulant accumulation at the membrane surface, and this resulted in no fluctuations of the flux (data not shown).

On the other hand, the fluxes varied significantly when the biofilms were developed under constant foulant load (Exp. B, Fig. 4 a). Just as the biofilm mass, the permeate fluxes depended on the biodegradability of the foulants and on their MW. The highest stable fluxes (around 6 L m^{-2} h^{-1}) were observed for the control and for the low MW nondegradable foulant (1 kDa PSS) that permeated through the biofilm-membrane composite. The fluxes measured with addition of Dex 1, 150, 2000 kDa stabilised at similar level of 3 L m^{-2} h^{-1}. The lowest flux was recorded for the high MW nondegradable foulant (80 kDa PSS) at a level of 2 L m^{-2} h^{-1}. Permeate fluxes monitored for short-term filtration in absence of biofilm are presented in Fig. 4 b. Overall, the permeate fluxes levels were lower than those monitored when biofilm formation was tolerated, independently of the foulant properties. Also, flux stabilisation was not always observed. A progressive flux decline was for recorded for the PSS 80 kDa foulant.

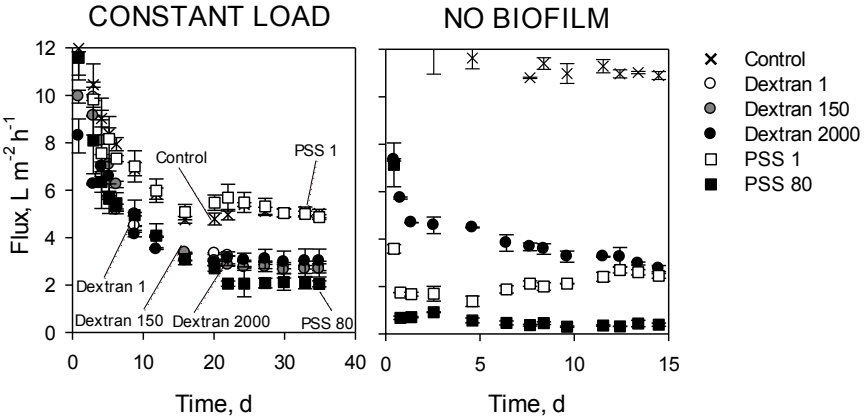

Figure 4 *Permeate flux for constant load (Exp. B), compared to flux without biofilm (Exp. C). Exp. B was conducted in prepared creek water, with 7 mg L^{-1} foulants added as product, while exp. C was conducted in deionised water, with 50 mg L^{-1} foulants added as product (25 mg L^{-1} as organic carbon). Each error bar indicates a standard deviation.*

Discussion

How does a biofilm on a membrane surface influence the foulant removal?

Biodegradable foulants

Our results show that the foulant removal level depended strongly on the foulant biodegradability, as well as its loading. For biodegradable foulants, the biofilm was able to hydrolyse (Fig. 3 e), and if exposed to the constant foulant loading during long term - degrade the foulant (Fig. 3 d). Both hydrolysis and degradation steps were captured by the chromatography analysis (Fig. 3). For example dextran 150 kDa (Fig. 3 a-d): on day 1 of filtration the removal of dextran 150 kDa was due to membrane retention capability. On day 3 hydrolysis of dextran 150 kDa was observed, and on day 9 dextran 150 kDa was completely degraded. Thus in our case biofilms exposed to the constant foulant loading were responsible for degradation of both low and high molecular weight biodegradable substrates (complementarily to the study of Kang et al. (2007)).

However, for the intermittent foulant presence in the filtration system, the biofilm could not degrade the foulants as efficiently. This resulted in hydrolysis (partial degradation) of the biodegradable substrates to lower MW fractions, which permeated through the membrane and lowered permeate quality (Fig. 2 a). The hydrolysis for both dextrans 150 and 2000 kDa for the unadapted biofilm is shown in Fig. 3 e. The less efficient foulant removal could have resulted from shorter exposure of the biofilms to these substances, thus insufficient contact time between the biofilm and the permeating foulant, or slower degradation kinetics due to different microorganisms. The capability of biomass to utilise the polymeric substrate was limited, and depended mainly on size and degradability of the foulants, as shown by Larsen and Harremoes (1994), Zhang and Huck (1996). Small biodegradable foulant (1 kDa Dex) was better degraded than large Dextrans (150, 2000 kDa). From bacterial metabolism point of view, the easier to degrade and smaller the substrate (molecular size), the faster it should be utilised. In our case it took around a week for the biofilm exposed to constant foulant loading (exp. B) to adapt and start fully degrading degradable Dextrans 150 and 2000 kDa. We can conclude that enzymatic pathways existed already, since hydrolysis in both exp. A and B was almost immediate, and deduct that bulk hydrolysis dominated in the GDM system (Larsen and Harremoes 1994), rather than substrate adsorption onto the biofilm (Bouwer 1987). The consequences of bulk hydrolysis would be exactly partial degradation of the foulant to smaller size fractions that would permeate

through the membrane, if the internal transport and utilisation rate within the biofilm itself was limited. If a nutrient limitation existed with respect to carbon:nitrogen:phosphorus (C:N:P) ratio in the feedwater, the organic substrate would also be hydrolysed and not fully uptaken by the bacteria due to the N, P nutrient limitation. In order to degrade fully, the bacteria would have needed to optimise their metabolism with respect to C:N:P ratio, such as switching to high affinity mechanisms to acquire limited nutrients, or to recycle the limited elements (Merchant and Helmann 2012).

In summary, for biofilms exposed to variable foulant loading hydrolysis of the foulants was dominant, as opposed to full degradation under constant foulant loading. The hydrolysis changed the molecular size of the foulant into smaller fractions that were able to permeate through the membrane, ultimately leading to permeate quality decline (Fig. 3 e). The hydrolysis step did not seem to be the limiting factor for full foulant degradation. The permeation rate and thus contact time between hydrolysed foulant and "biofilm-membrane" composite must have played a role in determining whether the foulant would be partially or fully degraded (Larsen and Harremoes 1994). The hydrolysed, permeating organic carbon could then become substrate for bacterial regrowth in the permeate water (Derlon et al. 2014). However, under constant foulant loading the biofilms were better adapted and able to degrade the organic model foulants directly on the membrane, without the need for pre-treatment, until no organic carbon from these foulants was present (Fig. 3 b, d). In this case removal of organic carbon with "biofilm-membrane" composite was considerably higher than for membrane only (Fig. 2 b).

In our study we tested model foulants with respect degradability and molecular weight, however in reality the natural organic matter (NOM) foulants are more complex with respect chemical composition and size (Frimmel 1998). The assimilable organic carbon (AOC), which is the easiest degradable fraction of NOM seems to be a major portion (50-70%) of low molecular weight NOM (below 1 kDa), in relatively clean surface waters (Hem and Efraimsen 2001). In this case AOC will be permeating through the UF membrane, but at the same time the biofilm growing on the membrane could degrade it since this is lowest molecular weight AOC. The more problematic will be AOC that is composed of higher molecular weight of 1-10 and above 10 kDa (Hem and Efraimsen 2001), which can also permeate through the UF membrane, but because of larger molecular size it might not be directly degradable by the biofilm. In this case biological pre- or post-treatment of the surface water is recommended in order to maximise AOC degradation and thus

reduce AOC passage through the biofilm-membrane composite (Derlon et al. 2014, Halle et al. 2009).

Nondegradable foulants

For nondegradable foulants, their retention depended on the foulant MW, as the biofilms were not able to uptake them as substrate for growth. Physical presence of the biofilm modified the retention capability of the pristine membrane (Fig. 2). The biofilm increased retention of low and high MW PSS by an average 10-20% in both experiments (Fig. 2 a, b) compared to the virgin membrane retention (similarly observed by Lu et al. (2013)). When the biofilms were physically removed (flushed off) from the membrane surface at the end of experiment, the retention of foulants comparable with the level of virgin membrane retention (Fig. 2, biofilm removal). This indicates that biofilm layer could efficiently act as a secondary layer, with better retention properties than the pristine membrane. The mechanisms of biofilm acting as a protective layer could include pore constriction (Sahar et al. 2011), increased repulsion forces (Lu et al. 2013) or postulated hindered diffusion (Shen et al. 2014). Whatever the main mechanism in our case, the level of foulant retention remained stable throughout the duration of the experiments (weeks).

How does a foulant type influence biofilm composition and permeate flux?

Permeate flux also depended on the foulant loading (constant or variable), as well as the foulant biodegradability. For the adapted biofilm case (constant loading), the degradable foulants induced additional biofilm growth (compared to control), which resulted in lowered permeate flux. The measured total solids (TS) and extracted proteins confirmed biofilm growth or foulant accumulation on the membrane surface (Table 2). Biodegradability of the foulant had the biggest influence on the flux. Biodegradable foulants provided more organic carbon for biofilm growth, which resulted in both increased biofilm mass (TS), as well as biofilm protein content. The highest fluxes were recorded for the low TS and low protein concentrations (control and PSS 1 kDa, Table 2). As shown by Dreszer et al. (2013), it is more biofilm EPS than bacterial cells that contribute most to resistance in membrane fouling. As discussed by Stewart (2012) the EPS does not have convective transport properties, hence its presence on membrane surface would be critical for lowering the permeation rates. Unfortunately, carbohydrate content of biofilms was not determined to assess influence of carbohydrates onto permeate flux, however it is not clear which part of biofilm EPS – carbohydrate (Cho and Fane 2002) or protein (Lee et al. 2003) play major role in membrane fouling. For nondegradable foulants, foulant molecular weight determined if it would

accumulate on the membrane surface or not (1 or 80 kDa PSS). The lowest permeate flux was recorded for the accumulating PSS 80 kDa, without additional carbon for biofilm growth (Table 2). In this case resistance to filtration caused by the accumulating foulant was highest, despite very low protein content of the biofilm.

We also compared the flux level from constant foulant addition (adapted biofilm, exp. B) with flux obtained in absence of the biofilm (exp. C) in Fig. 4. Without the biofilm present on the membrane surface, the flux level for the foulants tested (dextran 2000 kDa, PSS 1, 80 kDa) was considerably lower than when the biofilm was present (Fig. 4 a vs b). This indicates that the biofilms could positively act as a protective layer, reducing the fouling level of the membrane and in turn the resistance to filtration. Because the biofilm was tolerated on the membrane surface, it was able to degrade the dextran 2000 kDa in exp. B, thus preventing continuous foulant accumulation and flux decline (Fig. 4 a), contrary to flux in exp. C (Fig. 4 b). For nondegradable foulant PSS 80 kDa, the biofilm must have acted as a protective layer from direct membrane fouling, such as pore blocking or gelation of the accumulating PSS polymer. The curve of the flux for PSS 80 kDa in Fig. 4 b shows that fouling in absence of biofilm was immediate (flux went to almost zero after 1 day filtration). The comparison of flux between PSS in deionised water (in absence of biofilm) and in diluted creek water (in presence of the biofilm) is not exact, as no ions were present in deionised water, however typically in presence of the ions membrane fouling is more severe, due to electrostatic interactions between the particles (Bowen and Jenner 1995, Faibish et al. 1998).

Relevance

Biofouling is often seen as a "biofilm reactor in a wrong place" (Flemming et al. 1997). However, in our study we demonstrate that biofilms developed on ultrafiltration membrane were responsible for organic foulant degradation in situ. The biodegradable foulant (dextrans) allowed for more biofilm growth (represented by measured TS and protein). The additional biofilm growth resulted in lower permeate flux, compared to control and to nondegradable, low MW foulant (1 kDa PSS). However, the permeate flux loss was not significant compared to the gain in terms of permeate quality improvement. The presence of biofilms on membrane surfaces increased permeate stability by limiting organic carbon content and in turn potential bacterial regrowth in the permeate (Derlon et al. 2014). Furthermore, biofilm presence on the membrane surface stabilised the permeate flux when the influent contained nondegradable, accumulating foulant (80 kDa

PSS). In absence of the biofilm, considerable flux loss was observed during the short term experiment, compared to when the biofilm was present and protecting the membrane from further fouling (Fig. 4 a vs b).

Gravity Driven Membrane ultrafiltration, operated without electrical energy is a relevant solution for small scale water treatment systems. Currently the GDM systems are installed in developing countries (Boulestreau et al. 2012), where they are used for surface water filtration (pond, lake, river) with varying feed water quality. Chemical or physical pre-treatment of the feedwaters at the household level is unfeasible (scale and costs). Presence of the biofilms on the membrane surface can improve permeate quality due to degradation as well as increased retention of the foulants, therefore enhancing permeate stability. Thus in this context the biofouling can be redefined as a "protective biofilm in the right place".

The limitation of this approach lies in the biofilm activity, foulant concentration (loading) and type. If a very high load of degradable foulant enters the biofilm-membrane system, the biofilm might not be able to degrade it all in given timeframe. This would result in hydrolysis of the foulant into smaller fractions and their release into the permeate. Similar thing would happen if the foulant was slowly degradable, resulting in permeate quality decline. In these cases it might be beneficial to periodically remove the biofilm to eliminate the accumulating foulants, as well promote active biofilm growth.

Conclusions

We studied influence of biofilms growing on ultrafiltration membranes during long term GDM ultrafiltration on both permeate quality and quantity. The biofilms grown on the membrane surface were responsible for:

- degradation of LMW biodegradable substrates, which lead to direct improvement of permeate quality,
- hydrolysis of HMW substrates, when the biofilms were exposed to the foulant on an intermittent basis, which overall lead to a decline of permeate quality,
- hydrolysis and degradation of the foulants, when the biofilms were exposed to the foulant continuously, with constant loading (up to the tested influent concentration of 3.5 mgC L^{-1})
- permeate quality improvement for nondegradable foulants, due to physical retention in the biofilm
- prevention of permeate flux decline that would result from long term accumulation of nondegradable foulants.

When physical or chemical pre-treatment of raw waters is not feasible, it is beneficial to allow for biofilm establishment on the membrane surface for both foulant degradation and increased retention, resulting in permeate quality increase. Biofilm presence results in physical membrane protection from further fouling, resulting in stabilised permeate flux.

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Abbreviations

CWF	Clean Water Flux
Dex	Dextrans
DOC	Dissolved Organic Carbon
EPS	Extracellular Polymeric Substances
GDM	Gravity Driven Membrane
GPC	Gel Permeation Chromatography
HMW	High Molecular Weight
kDa	kilo Dalton
LC-OCD	Liquid Chromatography-Organic Carbon Detection
LMW	Low Molecular Weight
PBS	Phosphate buffered saline
PSS	Polystyrene sulfonate
SD	Standard Deviation
SEC	Size Exclusion Chromatography
TOC	Total Organic Carbon
TS	Total Solids
UF	Ultrafiltration
VS	Volatile Solids

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SUPPLEMENTARY INFORMATION

In Fig. S1 degradation of model foulants in a batch experiment is shown. The foulants were added into 1 litre of prefiltered creek water in completely mixed glass reactors (thermostated at 20°C). The initial concentration of foulants was 2.5 mgC L^{-1} and was monitored daily with TOC measurements.

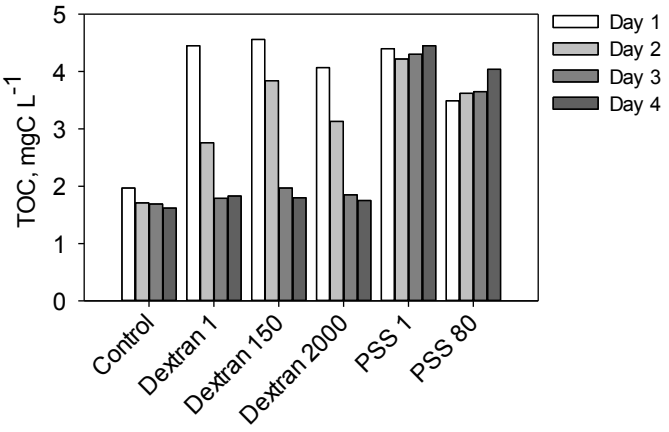

Figure S1 *Foulant degradation in a batch experiment. The foulants were added to continuously stirred, thermostated at 20°C glass vessels filled with 1 L prefiltered (0.4 μm) creek water. A TOC sample was taken and analyzed every day. TOC level in control is from creek water, as no foulant was added.*

Chapter 5

Conclusions and Outlook

In this thesis interactions between model inorganic, organic foulants (mimicking foulants present in surface waters) and biofilm development on ultrafiltration membranes were investigated. The specific focus was how the inorganic particles and organic substrates influence biofilm development and in turn resistance to filtration over long term dead-end filtration. Another focus was how presence of the biofilm influences quality of the produced permeate due to hydrolysis and degradation of the organic foulants.

Main conclusions of the individual chapters

Experiment with continuous long term (one month) dead-end ultrafiltration of prepared creek water and addition of high concentration of inorganic particles indicated that size and structure of the particles influenced biofilm structure (chapter 1). Fine and homogenous particles accumulation negatively influenced the biofilm structure by creating homogenous biofilm structure and thus bringing additional resistance to filtration. Larger, heterogeneous particles created more heterogeneous biofilm structure with less resistance (compared to when fine particles were present) and thus higher permeate flux. Therefore feedwater pre-treatment such as pre-sedimentation or pre-filtration could result in removal of the beneficial large particles, and thus lower fluxes.

Long term filtration of creek water with addition of degradable and nondegradable model organic polymers resulted in development of biofilms with different biomass (chapter 2). More biomass was grown in presence of the degradable substrates, compared to when no or non-degradable substrates were present. Additional biofilm growth due to degradable substrate resulted in lower fluxes, but at the same time when foulant loading was constant, the biofilm could degrade the degradable foulants leading to permeate quality improvement. When loading of the foulant was variable, the biofilm degraded the foulant only partially, leading to permeate quality decline. The partial degradation could be a result of insufficient contact time between biofilm and the organic foulant due to different permeation rates. Another possibility is that different biofilms developed with different microorganism composition and activity. For practical operation of the GDM, it is important to determine how to best operate the system in order to favour full degradation and permeate quality enhancement. Degradation capability by the biofilm will not only depend on the foulant biodegradability but also biofilm age and

thus activity. Hence minimising inert biomass accumulation on membrane surface that leads to biomass hydrolysis is essential in GDM dead end filtration.

Assimilable organic carbon (AOC) uptake and hydrolysis was also investigated in chapter 3. It was shown that biofilms growing on membranes can increase permeate quality by reducing the feed water AOC content. However over long term filtration (several months) permeate quality decreased due to hydrolysis processes within the biofilm, releasing the soluble organic carbon. Biological pre-treatment of the creek water using a packed bed biofilm reactor or slow sand filtration was shown to be a suitable approach to reduce AOC load and therefore limit the biofilm growth potential. However, the quality of permeate still could not be considered as biologically stable, as AOC level in permeate exceeded the concentration of 100 µg AOC L^{-1} (Hammes et al. 2010).

Outlook

Implications for gravity driven (low pressure) ultrafiltration treatment systems

The "biofilm-membrane" filtration approach is a promising alternative to produce water of drinking quality at minimum energy and chemical requirements, as opposed to membrane filtration only. Another advantage is permeate quality improvement due to increased retention and degradation of foulants by the biofilm. The disadvantages are decreased permeation rates (compared to traditional ultrafiltration systems) and possible permeate quality decline due to hydrolysis of the accumulated biomass, that ultimately ends up in the permeate. Hence further understanding how to operate the GDM system for optimising permeate quantity and quality for real applications is needed. The questions are on how to best operate GDM ultrafiltration system when inorganic particles are present. In particular, under what conditions the accumulation of particles is positive or detrimental to the filtration performance. Similarly, when organic matter is present in feedwater, how to operate the GDM system in order to favour full degradation of the organic matter by the biofilm rather than hydrolysis and leakage of hydrolysis products into the permeate (Derlon et al. 2014).

Within framework of the thesis interactions between biofilm and model organic foulants and inorganic particles were studied. The model foulants helped to identify possible negative and positive interactions between the biofilm-membrane-foulants, but they cannot substitute real contaminants present in feedwaters. It is

very probable that other interactions between biofilm (-membrane) -foulant could dominate in presence of the real foulants, depending on the foulant type and concentration, and feedwater characteristics such as pH and ionic strength. Additionally, sorption between organic and inorganic matter and sorption onto the membrane itself cannot be excluded, and was not investigated within scope of this thesis.

Building up a precise filtration model (i.e., for predicting permeate flux) may not be practical given the existence of different types of feedwaters and the high sensitivity to interactions between the foulants (Jermann et al. 2008, Van Den Berg and Smolders 1989). The model inorganic particles used with this thesis may not represent realistic interactions based on particles charge and sorption capability of organic matter. Similarly, the model organic foulants used in the studies represent easily degradable sugar based substrates, while organic matter present in real feedwater is more complex (Huber et al. 2011). However, if an attempt to build a model for predicting flux quantity and quality is made, then the model would need to investigate the following interactions in detail:

Feedwater composition: organic and inorganic matter type (size, charge) at different concentrations, pH and ionic strength

- Biofilm composition (EPS, presence of higher organisms i.e. grazers) and structure
- Biodegradability of organic compounds
- Sorption capability of organic matter onto the particles and the membrane

In order to study the influence of single components on permeate flux and quality, it would be recommended to: (1) extract real foulant fractions based on their size, charge, biodegradability (biopolymers, humic acids, building blocks, etc.) and (2) perform long term filtration with addition of these foulants in presence of diluted real feedwater background. In this way some interactions (i.e., degradation by biofilm, sorption, gelation of the macromolecules) between biofilm-membrane and the foulant(s) within real water background could be estimated.

Estimation of resistance to water flow

Quantifying resistance to filtration usually requires approximation and assumptions with respect to the structure of the fouling layers. While fouling layers are often modelled as homogenous species (particles, organic foulants), the biofilms form

stratified, heterogeneous layers (Derlon et al. 2012) of varying porosities and densities (Zhang and Bishop 1994). It is thus probable that overall resistance to filtration in presence of the biofilm cannot be approximated as homogenous layer and needs to be quantified more precisely. This would require quantifying resistance of each thin biofilm slice (thickness of few µm). Moreover, the resistances could change not only due to structure of the biofilm, but also its chemical composition (Kim et al. 2006). The composition of biofilm EPS may decide on the fouling and resistance (Cho and Fane 2002, Lee et al. 2003). Also, the mass transfer in biofilms is modelled as diffusion, but for heterogeneous biofilms diffusion is aided by convection (DeBeer et al. 1994, Lewandowski et al. 1995), although this is mostly for systems with shear. The difficulty is when to classify biofilms in GDM ultrafiltration as homogenous, and when as heterogeneous, and how to quantify the ratio of diffusion and convection within the biofilm in GDM.

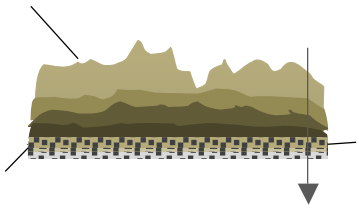

Figure 1 *Stratification and heterogeneity of the biofilm layers and of the resistances to filtration. The darker colour biofilm means higher resistance, with least resistive layers further away from the membrane surface. EPS sorption into the membrane pores itself cannot be excluded from estimating resistances to filtration.*

In GDM ultrafiltration it is unknown where the most resistive layers are situated. The resistive layers could be situated in the closest proximity to the membrane surface, with less resistive layers lying further away from the membrane and little impact on the permeation rates (as shown by Peter-Varbanets et al. (2011)), Fig.1. The resistive layers could also be stratified across the entire biofilm since no shear is applied during GDM ultrafiltration. To prove local resistance distribution in GDM, use of nondegradable, permeating through the membrane tracers would be recommended, with their in situ detection. Such method was proposed for single tube extractive membrane bioreactor and includes 1,1,2-trichloroethane (TCE) as tracer (Zhang et al. 1998), and perhaps could be adopted for GDM.

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