The Quest for a Universal Indicator for MBR Fouling

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ABSTRACT

During this study and with the objective of obtaining a significant database of comparable results from different membrane bioreactor units, a monitoring campaign was performed over one year in Berlin with four membrane bioreactor (MBR) systems. In these units, seventeen parameters were monitored on a weekly basis to characterise the mixed liquor. The objective was to evaluate the possibility of obtaining a universal parameter which could be used as a quick and easy indicator for short and long term fouling in MBR. For the measurement of the activated sludge filterability, an *in situ* filtration test cell was developed. The other parameters monitored were temperature, pH, capillary suction time (CST), time to filter (TTF), biopolymers, total organic carbon (TOC), chemical oxygen demand (COD), bound and soluble extracellular polymeric substances (EPS), bound and soluble transparent exopolymer particles (TEP), UV absortion of the mixed liquor supernatant, sludge volume index (SVI), nitrate, mixed liquor suspended solids (MLSS) and volatile mixed liquor suspended solids (MLVSS). The influence of the size of the foulants was also investigated via fractionation, in order to find the most relevant fraction for fouling. The relationship of the measured parameters and the filterability was evaluated with the statistical software SPSS using multiple linear regression. The results showed that the filterability of the activated sludge cannot be correlated with a unique parameter. TEP and the ratio between bound and soluble TEP appeared as the most interesting parameters using univariate analysis. Using multivariate analysis, critical flux was correlated with the parameters bound TEP, temperature of the mixed liquor, TEP (soluble) and nitrate with a regression coefficient of 95%. After fractionation, no sludge fraction could be identified as the most important for fouling in general terms.

Keywords: Membrane bioreactor – Fouling – Extracellular polymeric substances (EPS) – Transparent exolpolymer particles (TEP) – Critical flux

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NOMENCLATURE

Abbreviations

Abbreviation	Description	Units
ACS	Advanced control system	
BFM	Berlin filtration method	
bPR	Bound proteins	mg/L
BPC	Biopolymer cluster	
bPS	Bound polysaccharides	mg/L
bTEP	Bound TEP	mg/L
CAS	Conventional activated sludge	
CMC	Carboxymethylcellulose	
COD	Chemical oxygen demand	mg/L
coll	Colloidal	
CST	Capillary suction time	s
Df	Fractal dimension	
DFCm	Delft filtration characterization method	
DO	Dissolved oxygen	mg/L
DSVI	Diluted SVI	L/mg
EPS	Extracellular polymeric substances	mg/L
F/M	Feed to microorganism ratio	gCOD/(gMLVSS d)
HF	Hollow fibre	
J	Flux	$L/(m^2h)$
K	Permeability	$L/(m^2bar\ h)$
J_c	Critical flux	$L/(m^2h)$
J_{c-1}	Critical flux, previous data	$L/(m^2h)$
N	Number of samples	
MBR	Membrane bioreactor	
MF	Microfiltration	
MFI	Modified fouling index	s/L^2
MLSS	Mixed liquor suspended solids	g/L
MLVSS	Mixed liquor volatile suspended solids	g/L
MW	Molecular weight	kD
MWCO	Molecular weight cut off	kD

P	Pressure	mbar
P	Permeate	
PAN	Polyacrylonitrile	
p.e.	People equivalent	
PE	Polyethylene	
PES	Polysulfone	
PVDF	Polyvinylidene fluoride	
PR	Protein	mg/L
PS	Polysaccharide	mg/L
QCM-D	Quarz crystal microbalance with dissipation monitoring	
r	Pearson regression coefficient	
R	Resistance to filtration	m^{-1}
R_a	Resistance to filtration due to adsorption	m^{-1}
R_b	Resistance to filtration due to pore blocking	m^{-1}
R_c	Resistance to filtration due to cake layer	m^{-1}
R_i	Initial resistance to filtration	m^{-1}
R_m	Resistance of the membrane	m^{-1}
R_t	Total resistance to filtration	m^{-1}
RO	Reverse osmosis	
SMP	Soluble microbial products	mg/L
SRT	Sludge retention time	d
SPSS	Statistical package for the social sciences	
SVI	Sludge volume index	mL/mg
T	Temperature	ºC
TEP	Transparent exopolymer particles	mg/L
TMP	Transmembrane pressure	bar
TS	Total solids	g/L
TTF	Time to filter	s
TOC	Total organic carbon	mg/L
UF	Ultrafiltration	
UV	Ultraviolet absorbance	
VFM-MBR	VITO fouling measurement	
VFM_{rev}	Normalized reversible fouling value	%
XG	Xanthan gum	
VSS	Volatile suspended solids	g/L

Symbols

Symbol	Description	Units
α	Specific resistance	m/kg
μ	Dynamic viscosity	mPa s
ΔR_{20}	Filtration resistance measured with the DFCm	m^{-1}
R^2	Regression coefficient, multivariable analysis	

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1. INTRODUCTION

In the last decade, the membrane bioreactor (MBR) technology has become competitive for advanced treatment and recycling of industrial and municipal wastewater. Nevertheless, there are still some impediments for the spread implementation of this technology. One of the main obstacles for a wider acceptance of the MBR technology by the wastewater treatment market is the lack of design and method standardization in membrane bioreactor systems (de Wilde *et al*., 2009). This is actually not a hindrance of the technology itself, but a disadvantage caused by manufacturers and end-users and the lack of agreement between them. For instance, the absence of a standard method for the determination of the filterability of the activated sludge in MBR has led to the development of a large quantity of different and more or less elaborated filtration characterization methods in the last years by numerous research institutions and end-users working with this technology. Some of the well-established parameters in the conventional activated sludge (CAS) process used to determine the settleability of the sludge like sludge volume index (SVI) or capillary suction time (CST) and time to filter (TTF) for dewaterability measurement are only of limited use in MBRs as filterability indicators. Part of the know-how of the CAS technology can be applied to the membrane bioreactor process; however, the introduction of the membrane step complicates the process, converting membrane fouling in one of the greatest impediments for the implementation of this technology. There are also some specific methods to measure the fouling potential of feeds like the modified fouling index (MFI) (Schippers and Verdouw, 1980), but all of them, together with TTF, SVI and CST are based on dead-end filtration, meaning that the fouling mechanisms expected from this measurements are not representative of those occurring during cross-flow filtration, which is the operation mode of the MBRs. There is therefore a need for specific parameters which can provide valuable information about the fouling propensity of the activated sludge in order to be able to optimize the process.

After the work of Rosenberger *et al.* (2006), it was believed that the concentration of polysaccharides in the activated sludge filtrate could be the sought-after parameter which could be used as a "fouling indicator", as they found a linear relationship between this parameter and long-term fouling rates in two parallel membrane bioreactors. Numerous posterior studies tried to replicate the relationship and some of them succeeded, whereas others found no relationship between these two parameters Drews *et al*. (2008). Unfortunately, as all these studies are generally performed under different conditions (different membranes, sludge retention times, hydraulic conditions and different incoming wastewater), the results are rarely comparable.

The objective of this thesis was to evaluate the possibility of obtaining a universal parameter which could be used as a quick, easy indicator for short and long term fouling in MBR. Several studies have been previously performed in order to identify the main

fouling culprit (Liang *et al*., 2007; Kim and Nakhla, 2009; Rosenberger *et al*., 2006; Guglielmi *et al*., 2007; Lyko *et al.*, 2008). However, they used the plant data (permeability, fouling rates, etc.) to study the correlation between these and the parameters measured in the activated sludge. This avoids data comparability by using different MBRs with different module configurations, membrane materials and operational conditions. Instead of using plant data, Grelier *et al.* (2006) used a non-aerated external test cell to evaluate the fouling propensity of activated sludge in three MBR pilot plants of 70 L during one year. In this study, an aerated test cell was especially designed and constructed for simulating a real MBR operation and measuring filterability directly in the MBR tanks. Using this novel test cell, the filterability of four MBR units at pilot scale was evaluated over 10 months. In these units, seventeen parameters were monitored on a weekly basis over ten months in order to characterise the mixed liquor. To the knowledge of the author such a comprehensive monitoring campaign was never performed before and it provided valuable information about the contribution of the different parameters to the fouling propensity of activated sludge in MBR.

2. STRUCTURE OF THE THESIS

A schematic outline for the studies performed during this thesis is represented in Fig. 1. With the objective of evaluating the possibility of obtaining a universal parameter for different MBRs which could be used as an indicator for fouling in MBR, an intensive monitoring campaign was carried out in four MBR units on a weekly basis. This included the monitoring of the filterability of the activated sludge and the measurement of the sludge characteristics. Additionally to the here called "classical parameters", commonly measured in fouling investigations, the transparent exopolymer particles (TEP) were measured for the first time in an MBR system within this study. The resulting set of data was statistically analysed using univariate and multivariate analysis in order to investigate the relative influence of the studied parameters on activated sludge filterability. For the measurement of the sludge filterability, an innovative *in situ* test cell for the determination of critical flux (J_c) was designed and constructed during the project and a novel filtration characterisation method, the Berlin Filtration Method (BFM), was developed in order to follow-up the filterability of sludge in the MBR units. The selection and development of novel methods in the monitoring campaign (TEP and BFM) required the execution of preliminary studies. In the case of the TEP, filterability studies with model solutions of polysaccharides were carried out and several parameters were assessed in order to relate the characteristics of the different polysaccharides (especially TEP concentration) with their fouling propensity. Besides, a preliminary study was carried out to validate the BFM against existing filtration methods.

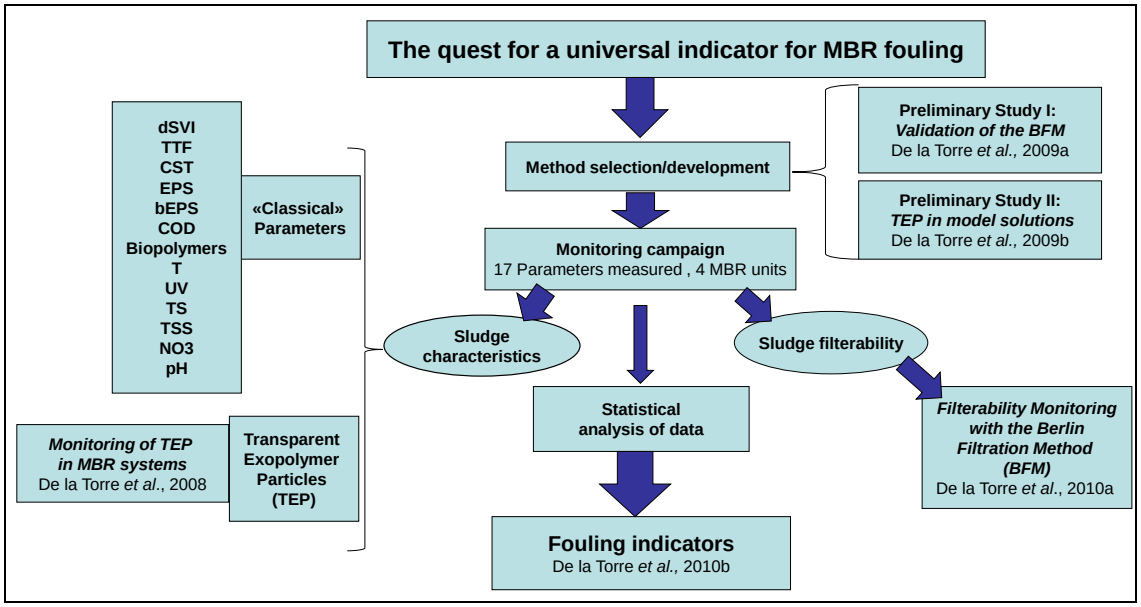

Fig. 1. Structure of the thesis.

3. BACKGROUND

3.1. MEMBRANE TECHNOLOGY

Membrane technology is based on the use of a semipermeable membrane for separation. In water technology, membrane filtration has gained importance in the last decades, being a key step in many water and wastewater treatment processes.

In MBR technology, the secondary clarifier is substituted by a membrane, normally in the range of micro- or ultrafiltration, which accomplishes the separation of the biomass from the treated water. Cross-flow is the filtration mode generally employed, using air scouring in order to avoid severe accumulation of particles on the membrane. Organic membranes are preferred over the ceramic ones, and commonly used materials are polyvinylidene fluoride (PVDF), polyethylene (PE), polyethersulfone (PES) and polyacrylonitrile (PAN). The process operates at low pressure and filtration is generally carried out at constant flux.

The driven force of the process is, as represented in Fig. 2, the so-called transmembrane pressure (TMP).

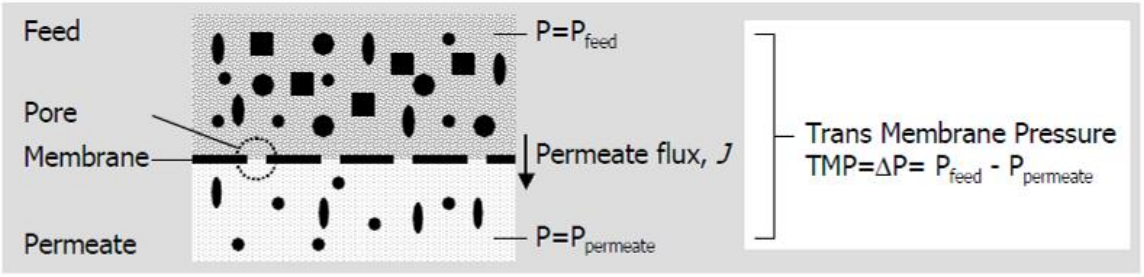

Fig. 2. Membrane filtration by Evenblij (2006).

Basic parameters in MBR operation are the permeability and filtration resistance, defined as follows:

$$\text{Permeability} \qquad K = \frac{J}{TMP} \qquad [1]$$

$$\text{Filtration Resistance} \qquad R = \frac{TMP}{J \cdot \mu} \qquad [2]$$

Where J is the flux, and μ is the viscosity of the permeate.

3.2. MEMBRANE BIOREACTORS

Membrane bioreactors are a smart combination of conventional activated sludge technology and membrane filtration. Some advantages presented by this technology are the low footprint required due to the absence of the secondary clarifier and the high effluent quality obtained which is practically free from particles and microorganisms and enables the effluent to be reused for numerous purposes. Furthermore, whereas the effluent quality from the conventional activated sludge technology is highly dependent on the process operation, the MBR technology offers a robust system in terms of effluent quality, which constantly meets the European bathing water quality standards.

The more stringent effluent quality regulations and the increasing importance of water reuse due to an overexploitation of water resources and urban development have boosted the construction of new MBR plants in the last years. The rapid evolution of the MBR market in Europe until 2008 can be observed clearly in Fig. 3. Within a decade, the constructed systems increased in size from few thousands of people equivalent (p.e.) up to large plants serving more than 100.000 p.e., demonstrating that MBR has become a technology of choice also in large wastewater treatment installations (Lesjean et al., 2011).

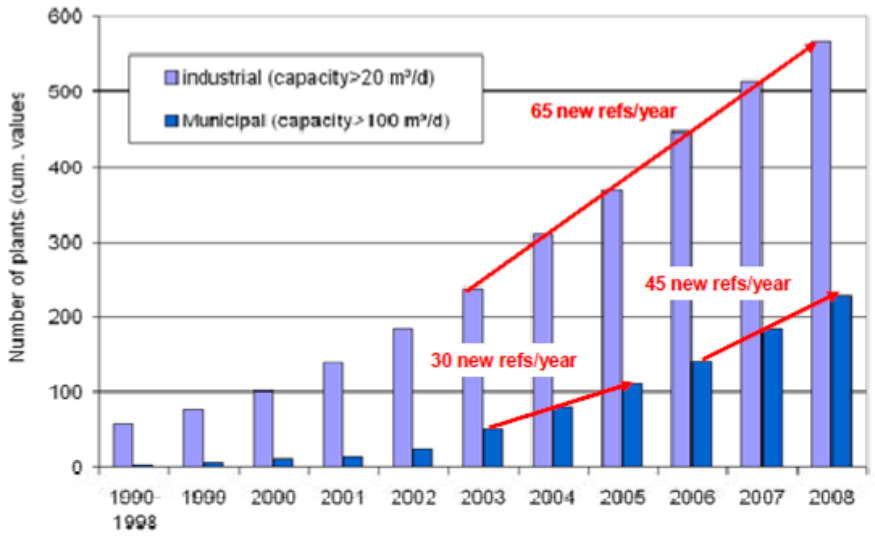

Fig. 3. Evolution the MBR market in Europe (Huisjes *et al*., 2009).

On the other hand, the MBR presents important disadvantages like high capital and operational costs, which are still significantly higher than those of the CAS. This is mainly due to membrane installation and replacement costs and the high energy consumption of the process due to air scouring, which is necessary to control membrane fouling (Verrecht *et al*., 2010). The fouling problematic will be deeply discussed in section 3.3.

The first generation of MBR were external, where the membrane was part of a side-stream unit. Twenty years ago, a new generation of MBR units appeared, based on the so-called immersed filtration system, working with low negative pressure (out-to-in permeate suction) and membrane aeration to reduce fouling. This resulted in capital and operation cost savings, which rendered the technology commercially viable for the municipal and

domestic wastewater (Lesjean *et al.*, 2009). Fig. 4 represents the two configurations: external and immersed.

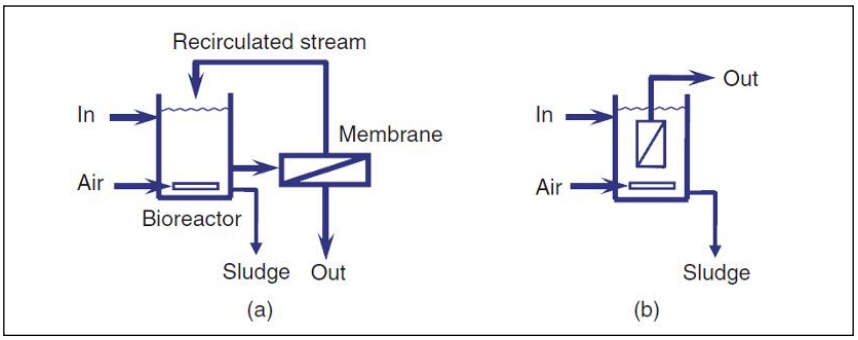

Fig. 4. Configuration of a membrane bioreactor: (a) sidestream and (b) immersed (Judd, 2006).

The external configuration entails the use of tubular membranes, which are located inside a support tube. Although it is generally assumed that the use of external modules implies high energy consumption due to sludge pumping, Norit X-Flow reports an energy consumption of less than 0.2 kWh/m^3 for different plants using their external membrane modules Norit Airlift which is an important improvement compared to the 3 – 4 kWh/m^3 reported for classical cross flow operation (Beforth *et al.*, 2009).

In the immersed-system market two main module types can be differenciated: hollow-fiber and flat-sheet. Working with hollow fibers permits backwashing in order to control membrane fouling whereas flat-sheet membranes do not generally allow this practise. However, Microdyn-Nadir commercialises flat-sheet membranes which can be subjected to backwash (Krause *et al.*, 2008). Fig. 5 illustrates the two types of submerged modules as well as the external tubular membranes from various commercial suppliers.

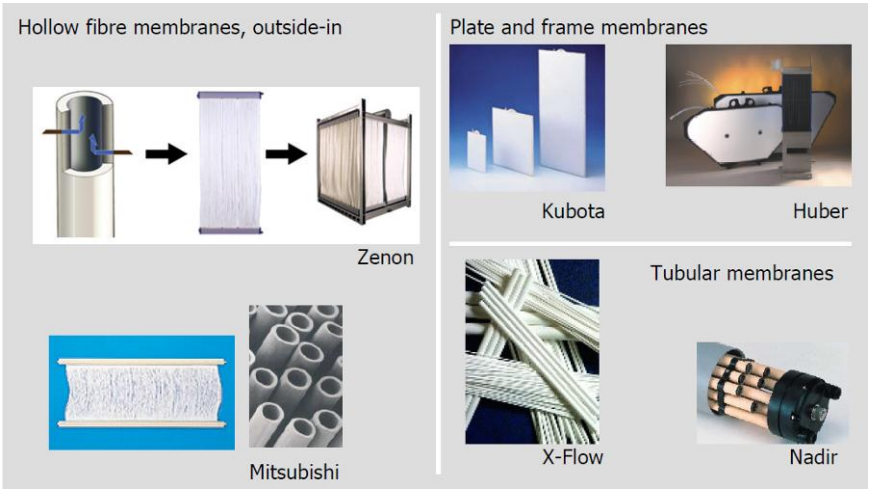

Fig. 5. Types of membrane modules used in MBR systems (Evenblij *et al.*, 2006).

3.3. FOULING IN MEMBRANE BIOREACTORS

Fouling is an intrinsic problem associated with all membrane processes. The extent to which fouling can be controlled is strongly related to the understanding of the mechanisms that govern this process and the compounds that promote it. Fouling of ultrafiltration (UF) membranes during, e.g., apple juice processing is mainly a consequence of the retention of carbohydrates, polyphenols and/or proteins (De Bruijn and Bórquez, 2006). In wine treatment, membrane fouling is primarily due to the accumulation of macromolecular or colloidal compounds (such as proteins and polyphenols) (Salazar *et al*., 2007). Fouling of ultrafiltration membranes in milk industries is mostly caused by precipitation of microorganisms, proteins, fats and minerals on the membrane surfaces (Mohammadi *et al*., 2003). When studying the fouling layer built after membrane filtration of beer, Taylor *et al*. (2001) concluded that, for all beers tested, the fouling layer consists of both protein-polyphenol complexes and carbohydrate gels. Unfortunately for the membrane bioreactor technology, the complexity of the mixed liquor makes the fouling process still not well understood to date, despite huge R&D efforts.

The topic of fouling has been intensively studied in the last years. It was reviewed in 2006 by Judd, Le-Clech *et al*., and more recently by Meng *et al.* (2009) and Drews (2010). When we take a look at the "word cloud" (Fig. 6), produced from keywords taken from scientific articles related to MBR, it can be clearly seen that the fouling issue is still a matter of study.

Fig. 6 Word cloud produced from MBR research keywords (Santos *et al*., 2011).

Fouling is not only a topic of interest in the research community but also between practitioners. Santos *et al.* (2011) interviewed 65 practitioners of MBR including technology suppliers, product suppliers, end-users and consultants trying to identify the main technical problems in MBR. From 48 respondents, 15% of them answered that fouling is their biggest concern when treating with MBR. This is shown in Fig. 7.

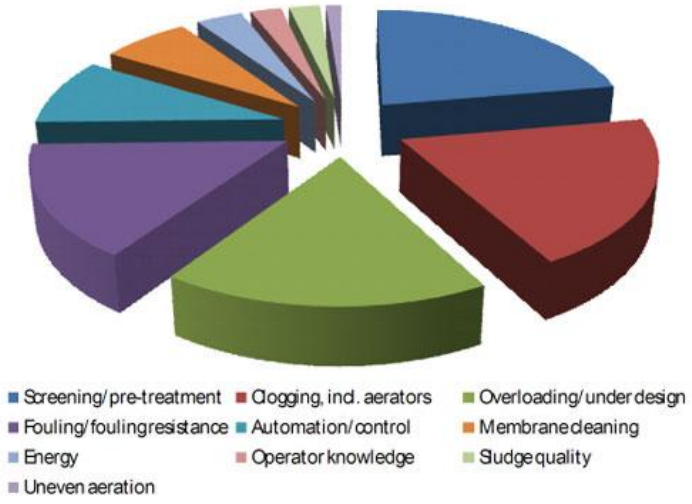

Fig. 7. Main topics identified from the practicioner survey (Santos *et al.*, 2010).

The term fouling is used to describe the deposition of constituents on the membrane, caused by an accumulation of matter, namely colloidal, particulate and solute materials, which may or may not be of microbial origin (such as extracellular polymeric substances (EPS)) (Judd, 2005). In Fig. 8 the different fouling mechanisms encountered in a membrane process are represented.

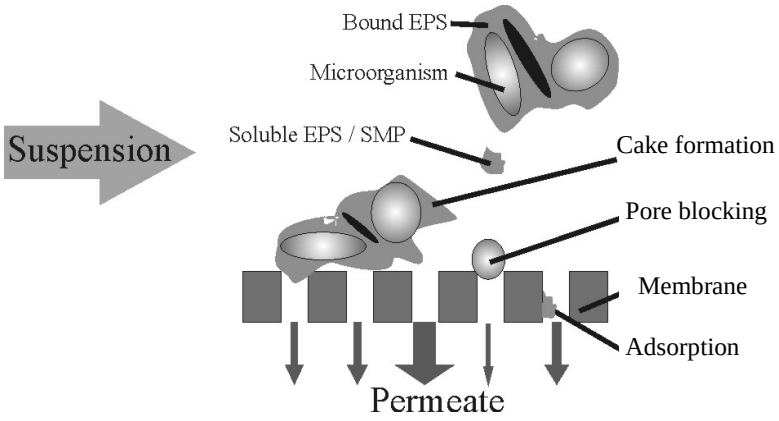

Fig. 8. Fouling mechanisms in membrane filtration (adapted from Iversen, 2010).

These are adsorption, pore blocking and cake layer formation. Additionally to this classification, fouling can be divided into reversible and irreversible. Fouling which can be removed with an appropriate physical protocol (like air scouring or backwashing) is normally called *reversible*. On the other hand, fouling which is not removed by mechanical means is considered *irreversible* and is generally only removed by chemical cleaning (Chang *et al.*, 2002). This comprises fouling caused by pore blocking, internal fouling caused by adsorption of dissolved matter into the membrane pores and part of the cake layer, which is not removed by physical means. A refined classification was introduced by Kraume *et al.* (2009) who distinguish four types of fouling: cake fouling (removed by

mechanical means), residual fouling (removed with maintenance cleanings), irreversible fouling (removed with recovery cleanings) and the long-term irrecoverable fouling of the membrane, which resists both chemical and mechanical means.

As a conventional membrane bioreactor is generally operated at constant flux, this accumulation of matter in and on the membrane causes an increase in the transmembrane pressure (TMP). That leads to an increase in chemical cleaning frequency and operational costs. If the correlation between flux and fouling rate was known, an optimisation could be performed but, as the rate of fouling depends on many inter-related variables and their relationship is still not clear, this optimisation cannot be performed yet (Drews, 2010). These variables which influence fouling are broadly categorised by Chang *et al.* (2002) into 3 main groups:

a) Membrane characteristics, such as the configuration, material, pore size, etc.
b) Operating conditions, such as the aeration, sludge age (SRT), flux.
c) The activated sludge, comprising the MLSS, feed composition, floc structure, floc size etc.

Furthermore, there are also interactions between these groups and the influence of a parameter may depend on the value of the parameters of other groups. For instance, and as it will be described in the following chapter, Drews et al. (2010) suggested that the polysaccharide content of the activated sludge filtrate seemed to correlate with fouling only when hollow fibers with larger pores are used.

As the final goal of this thesis is to obtain a measurable parameter in the activated sludge which can be used as a fouling indicator, the most important point of these three for the present study will be point c). For this reason the influence of the other two points (influence of membrane material and operating conditions) will not be further discussed. Within point c), the feed composition variable will be limited in this thesis to municipal and domestic wastewater. Regarding the influence of activated sludge characteristics on fouling, this will be reviewed in the following section.

3.3.1.FOULING AND ACTIVATED SLUDGE CHARACTERISTICS

It is generally acknowledged that activated sludge can be fractionised into 3 main components: colloids, suspended solids and solutes (Flemming and Wingender, 2001). Bouhabila *et al*., (2001) noted that colloids and solutes play an important role in membrane fouling when using hollow fibre membranes with both real and synthetic sludge in MBR units at lab and pilot scale. They reported a contribution of the colloidal and soluble fractions of about 75% to membrane fouling, and the specific resistance when filtering these fractions was about 10 times higher than that of total sludge. This has been supported by other authors, who have attributed the higher permeability presented by the total sludge to the formation of a “secondary dynamic membrane” constituted by the sludge flocs that

entraps potential foulants and prevents the membrane from internal fouling (Le-Clech *et al*., 2006; Van den Broek *et al.,* 2010). This was confirmed by Wu *et al.* (2012) using a lab-scale MBR and different membrane modules and working at different EPS and TEP concentrations. The conclusion was that as the soluble EPS and TEP in the activated sludge of the MBR increased, those membranes which were clean and did not possess a built cake layer were more affected by fouling than those with an established cake layer, demonstrating that the cake layer helps avoiding membrane fouling.

There exists a wide diversity of results about the main fraction contributing to fouling: Wisniewski and Grasmick (1998) found that half of the filtration resistance was due to the solutes when filtering a biological suspension. Defrance *et al*. (2000) pointed at the suspended solids as major foulants when using an external ceramic membrane to filter activated sludge fed with real wastewater. A literature review of the contribution of sludge fractions to fouling was performed by Judd (2006) and is presented in Fig. 9, which illustrates very clearly the controversy of finding out the fouling culprit fraction. The reason for this may be that the three components suspended solids, colloids and solutes all play their roles individually but also forming complexes with other foulants, which complicates the understanding of the fouling mechanisms. Furthermore, fouling studies are in many cases performed in different conditions (membrane material, configuration, operational conditions and in this case, different methods of fractionation), which makes comparison within studies a difficult task.

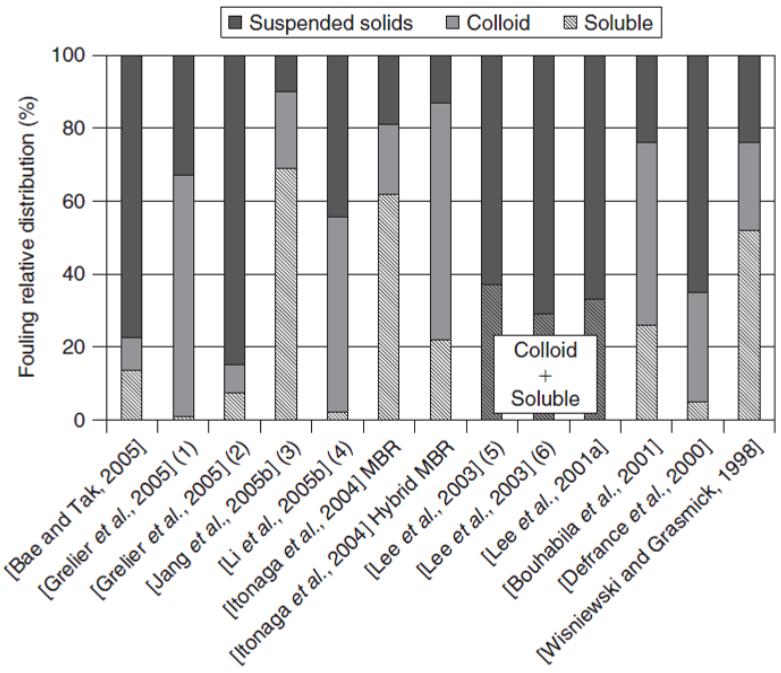

Fig. 9. Review of the contribution of the sludge fractions to fouling by Judd (2006). (1-2) For SRT increase from 8 (1) to 40 d. (2). (3) F/M of 0.5, results based on MFI. (4) Based on flux reduction after 600 min of each fraction filtration. (5-6) For SRT increase from 20 (5) to 60 d. (6).

In order to obtain a general picture of the relative influence of sludge characteristics in the fouling problematic, a review of several sludge characteristics is presented below. In addition to the commonly studied parameters like EPS, temperature or MLSS, the transparent exopolymer particles are included in this review as they were analysed for the first time in a wastewater system within this study and are presented here as a novel parameter for fouling investigations.

3.3.1.1. EXTRACELLULAR POLYMERIC SUBSTANCES (EPS)

According to Flemming *et al.* (2001), EPS is a general term used for macromolecules such as polysaccharides (PS), proteins (PR), nucleic acids, (phosphor-) lipids and other polymeric compounds found in or outside the cell surface and in intercellular space of microbial aggregates. As polysaccharides and proteins constitute the main components of EPS, these are normally quantified as the sum of these two groups. The soluble fraction of EPS is called soluble microbial products (SMP), and it is obtained by filtration or centrifugation of the activated sludge sample.

Due to its gel-like and sticky nature, there are evidences that the EPS matrix might be responsible for forming a barrier to permeate flow. Rosenberger *et al.* (2006) observed a linear relationship between MBR fouling and polysaccharide concentration at 8 d SRT in the sludge water phase and no clear correlation with other parameters like MLSS, chemical oxygen demand (COD), total organic carbon (TOC) or protein in the sludge waste. The relationship was more pronounced when SRT was 8 d than at higher SRT (15 d). This was supported by Liang *et al*. (2007), who investigated fouling with synthetic wastewater treated in a lab-scale MBR at 10, 20 and 40 d and reported a more pronounced accumulation of EPS at short SRT. An important conclusion of their study was that although the accumulation of EPS was higher at shorter SRT, the proportions of SMP with large molecular weight in supernatant and effluent were quite similar, so that an increased membrane sieving was not the cause of the more pronounced accumulation of EPS.

Drews (2010) reviewed several studies dealing with fouling and PS content and concluded that the correlation found by Rosenberger et al. (2006) between SMP and fouling can only be found in some studies, mainly when using hollow fibers with larger pores. This was attributed to the effect of backwashing, which partially controls cake fouling, whereas in flat sheet modules (which operate without backwashing) the cake building on the membrane may be the predominant fouling mechanism. The fact that larger pores are more prone to fouling than narrow pores can be easily explained if we consider that the accessibility of SMP to the pores is much higher when using larger pores (microfiltration). In their studies, Drews *et al.* (2008) also observed that the level of SMP concentrations in lab and pilot plants is often significantly higher than in full-scale plants, which affects data comparison. Working with a standard equipment and protocol, a recent study evaluated fouling propensity of sludge from several MBR units throughout Europe concluded that no general correlation can be assumed for SMP and fouling (Moreau *et al*., 2010). In order to

clarify whether SMP are relevant for fouling or not, Wang *et al.* (2012) operated two MBRs in parallel in which SMP had been partially removed from the activated sludge treated by one of the MBRs. They found much lower TMP in the operation of the MBR where SMP had been excluded and concluded thus that they do play an important role in membrane fouling. A reasonable explanation of this controversy could be that, although EPS concentration correlates with membrane fouling, in some cases this correlation is diffuse because of the influence of other relevant parameters in the fouling phenomenon.

An important factor that plays a role in EPS fouling is the food to microorganism ratio (F/M). Some studies (Trussel et al. (2006); Rosenberger et al. (2006)) found a clear relationship between fouling rates and F/M ratio which was associated to the influence of this parameter on EPS. The reason for this correlation might be a change in the nature of the SMP, as it has been reported that they have a wide spectrum of molecular weight and their apparent molecular weight distribution is affected by both SRT and feed to microorganism ratio (F/M) (Barker and Stuckey, 1999). EPS is a very generic term; they show a very broad diversity of properties and nature. Keeping this in mind, besides the influence of parameters like ionic strength and pH, one of the reasons for the contradictory results when trying to correlate fouling with total EPS concentrations could be this diversity of nature; some specific EPS could possess thus greater propensity to foul the membrane than other EPS groups. Liao et al. (2001) studied sludge flocculation and settleability and confirmed that not only the quantity but also the quality of the EPS is a determinant factor for flocculation. Miyoshi et al. (2010) tried to elucidate the influence of EPS nature on fouling by extracting different fractions of polysaccharides using lectin affinity chromatography from a mixed liquor suspension. After the separation, they performed filtration experiments in order to evaluate the fouling propensity of each fraction and reported very different fouling potential for each fraction. In order to study the influence of EPS size on fouling, Arabi and Nakhla (2010) fractionated the activated sludge using membranes with molecular weight cut off (MWCO) of 1, 10, and 100 kD and evaluated the SMP content of the different fractions. They concluded that the fraction of 10-100 kD was the most important for fouling. Own filtration experiments (De la Torre et al., 2009) using model polysaccharide suspensions reported important differences in the fouling propensity of different polysaccharides, which were attributed to differences in charge density of the polymers and their gelling capacity. These results are further described in chapter 4.1.2. Other studies about EPS properties and fouling were performed by Sweity et al. (2011), who evaluated the adherence and viscoelasticity of adsorbed EPS layers from a fouled membrane using quartz crystal microbalance with dissipation monitoring (QCM-D). They pointed at the EPS layer fluidity as the key characteristic for fouling studies and proposed that the more fluidic the EPS layers are, the higher their accessibility to the membrane pores is, which allows them to penetrate and block the pores.

The presence of metal ions in the activated sludge has been also shown to play a role in the fouling problematic. Wang and Waite (2008) performed experiments with model solutions in order to test the influence of Ca and Na ions on EPS fouling and found out that some polysaccharides like alginate increased their fouling capacity in the presence of calcium

ions, whereas the concentration of Na ions did not influence the filtration resistance of the model solution.

Besides all these parameters influencing EPS fouling, there exists a relationship between nitrate concentrations and EPS, where PS concentrations have already been reported to clearly decrease with increased nitrate concentration, and especially protein rejection was found to be influenced by the concentrations of NH_4 and nitrite and by the rate of NH_4 oxidation. High rejection and at the same time low fouling was observed when, e.g., the level of nitrite was high (Drews *et al*., 2007).

Other parameters have been studied by some authors (Yao et al., 2011) like the influence of the protein to carbohydrate ratio (PR/PS) in EPS on fouling. They reported that a high PR/PS is beneficial for filterability.

In the last years several publications (Wang and Li., 2008; Sun *et al*., 2008; Wang *et al*., 2011) have reported the existence of biopolymer clusters (BPC), which are formed by aggregation of SMP and are much larger than these and independent of sludge flocs and EPS. The results of these publications show that BPC behave as a glue to facilitate the cake layer, resulting in serious MBR fouling.

3.3.1.2. TRANSPARENT EXOPOLYMER PARTICLES (TEP)

EPS are not only important when dealing with membrane systems; they are relevant in several other fields like flocculation, oceanography or seawater desalination. In these last two fields, the transparent exopolymer particles, one fraction of EPS, have received increasing attention in the last decade. They are found abundantly in the ocean and play an important role in many fields of marine ecology. Alldredge *et al.* (1993) performed coagulation experiments that revealed that TEP are major agents in the aggregation of marine phytoplankton. This process is important as they remove dissolved inorganic carbon from the upper ocean through photosynthesis and redirect it by sedimentation into the deep ocean (Engel and Passow, 2001).

TEP are sticky particles that exhibit the characteristics of gels, and consist predominantly of acidic polysaccharides (Passow, 2002). When Alldredge *et al.* (1993) analysed their seawater samples, 24-68% of the bacteria in the samples were attached to TEP. After they are stained with alcian blue, they can be observed as discrete deformable strings, disks or films up to several 100 μm long (Passow and Alldredge, 1995). In Fig. 10, alcian blue stained TEP can be observed from a freshwater sample.

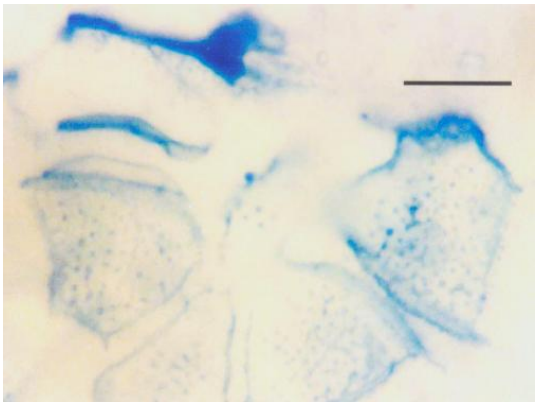

Fig. 10. Examples of TEP in detrital material from dinoflagellate algal bloom in a freshwater lake (Lake Kinneret, Israel). Bar = 5µm. (Berman and Holenberg (2005)).

The precise chemical composition of TEP is unknown, but it is known to be highly variable, because the chemical composition of TEP (and their precursors) depends on the species releasing them and the prevailing growth conditions (Passow and Alldredge, 1994). Engel and Passow (2001) investigated the C and N content of TEP in seawater obtained from several marine phytoplankton species. They found a correlation between TEP and C, but this correlation was different for each species of phytoplankton investigated. They reported a mean molar C:N ratio of 26.

TEP is measured using alcian blue, a cationic dye which binds to carboxyl (COO-) and to half-ester sulfate (OSO_3-) reactive groups of acidic polysaccharides. It can be quantified by microscopical enumeration (Alldredge *et al*., 1993) or spectrophotometrically. Passow and Alldredge (1994) developed the first semi-quantitative method using colorimetry, which is the base for all posterior methods for quantifying TEP, as it is rather less laborious than light microscopy enumeration. They use filtration of 0.4 µm pore size to separate the TEP from the seawater matrix and avoid interferences in the measurement. After filtration, they stain the filter with alcian blue and afterwards the filter is soaked in sulfuric acid for 2 h. After soaking, the absorbance of the acid solution is measured, and this absorbance decreases as the concentration of TEP in the solution increases following Lambert-Beer law. They performed comparisons and found that TEP measured spectrophotometrically compares well with parallel light microscope counts. They also reported the selectivity of the method demonstrating that neither proteins nor neutral polysaccharide bind alcian blue (Passow and Alldredge, 1995). In former studies, Rasmus *et al.* (1977) showed that the amount of adsorbed alcian blue is directly related to the weight of the exopolymer but it also depends on the anion density of the exopolymer. The consequence is that the method is not truly quantitative as it can only measure the staining capacity. Calibration is normally performed with Xanthan gum, which is an acidic polysaccharide and that permits expressing TEP concentration on a weight basis (mg/L xanthan equivalent).

Several modifications of the method developed by Passow and Alldredge (1994) have been performed. Thornton *et al.* (2007) adapted the method using dialysis in order to desalt marine samples (and standards made up in seawater) before analysis. Villacorte *et al.* (2009a, 2009b) extended the method to TEP in the colloidal range (0.05-0.4 µm) in order

to measure it in reverse osmosis plants. An alternative method to that of Passow and Alldregde (1995) was described by Arruda *et al*. (2004), who used centrifugation for the separation of the TEP-alcian blue complex and measured the absorbance of the supernatant. By using centrifugation, the interference of salts hinders the use of this method for the determination of TEP in seawater.

Some authors distinguish between colloidal TEP (from 0.05-0.4 μm) and particulate TEP (>0.40 μm) (Villacorte *et al.*, 2009b). Results show that colloidal TEP (82-93%) are more abundant than particulate TEP (7-18%) in both fresh water and sea water (Villacorte *et al.*, 2010a). This was confirmed by Van Nevel *et al.* (2012), who found that colloidal TEP accounted in both systems for 94-98% of total TEP. In other studies, Villacorte *et al.* (2010b) performed TEP fractionation with filters of 0.05, 0.10, 0.2, 0.4 μm and measured TEP in the different fractions, concluding that the main present fraction was the 0.05-0.1 μm fraction.

TEP analysis has been for the first time applied to the wastewater treatment technology in 2008 within this study (De la Torre *et al*., 2008). After this, recent studies by Wu et al. (2012) have evaluated the TEP content in a lab-scale MBR fed with synthetic wastewater using different membrane modules. However, the relationship between TEP and fouling had already been mentioned in 2005. It was Berman and Holenberg (2005) who proposed at that time that TEP in source waters might be a prime factor leading to biofilm growth on membrane surfaces and suggested measuring TEP concentrations to determine the efficiency of pre-filtration arrays upstream from high pressure membranes. In order to experimentally demonstrate this hypothesis, Berman *et al.* (2010; 2011) evaluated the fouling rate obtained by filtration of surface water samples containing different TEP concentrations using a cross-flow filtration array. The results showed that TEP concentration of the solutions correlated significantly with the fouling rate encountered. Moreover, they evaluated the role of bacteria in UF biofilm formation by comparing the evolution of a biofilm originated from feedwater with TEP and inactivated bacteria and another originated from feedwater with TEP and active bacteria. The biofilm formed after 50 h of filtration of the feedwater sample with active bacteria did not differ significantly to the biofilm formed after filtration of the feedwater containing active bacteria. The results showed that the majority of the EPS of the biofilm derived from TEP in the feedwater rather than from bacteria which adhered to the surface. The fact that TEP plays a relevant role in membrane biofilm formation had been already demonstrated by Bar-Zeev *et al*. (2009) who studied the evolution of TEP and bacteria in glass slides, in order to evaluate the implication of TEP in biofilm formation. The results showed that those areas of the glass slides attached with TEP became the main areas colonised by bacteria. From these results they concluded that TEP indeed played a relevant role in the early-stage biofilm formation. In recent studies (Bar-Zeev *et al.*, 2012) they supported these findings by observing the evolution of biofilm using confocal laser scanning microscopy, atomic force microscopy and bright field and epifluorescent microscopy.

Villacorte *et al.* (2009a) analysed TEP in the pretreatment, raw water and reverse osmosis (RO) systems of several integrated membrane installations. In their studies, ultrafiltration

proved to be most effective in removing particulate TEP in comparison to any other type of pre-treatment investigated (microfiltration (MF), conventional treatment), but neither low pressure membranes (MF/UF) nor conventional pre-treatments were absolute barriers against colloidal TEP from entering the RO system. They analysed TEP in the feed water and RO concentrates and, by assuming a complete rejection of TEP, they performed a mass balance and calculated the TEP accumulated on the membrane, which gave the deposition rates. They found important deposition rates in the RO membranes (around 30-70% of TEP from the feedwater) and this fact was verified by performing autopsies to the membranes. However, they admit that some of these substances may have been produced locally by biofilm bacteria and not from the feedwater.

Further studies have been performed in order to evaluate the elimination of TEP in the pretreatment of desalination plants. Kennedy *et al*. (2009) studied the removal of TEP in integrated membrane systems. Applying in-line coagulation at different dosage rates, they reported an elimination of 70% of the TEP greater than 0.4 micrometer with high dosage, whereas only 27% was eliminated working with a low dosage of coagulant. Other studies about the efficiency of TEP removal by the pretreatment of a desalination plant were performed by Bar-Zeev *et al*. (2009), who found that although the silt density index (SDI) was reduced up to 90%, the TEP after the pretreatment was removed only up to 30%. Van Nevel *et al.,* (2012) measured TEP in several points of two drinking water systems with different treatment schemes. They reported a removal rate of 67% of TEP by coagulation followed by sand filtration. When applying UF+RO, TEP were totally removed. In all treatment schemes, the levels of TEP were below the detection limits in the final drinking water.

An important link between TEP and fouling was recently shown by Schurer *et al.* (2012), who found high TEP levels during algal bloom which were in agreement with the high UF fouling rates encountered in an UF-RO seawater desalination plant. However, moderate occurrences of TEP in a different monitoring period did not noticeably affect UF performance. The TEP increase during algal bloom coincided with an increase in TOC and chlorophyll a (Villacorte *et al*., 2010a). The severe fouling was mitigated by applying in-line coagulation before the UF, which reduced significantly the irreversible fouling. However, the RO system did not show a decrease in normalized flux during the 4 months of operation of the plant (Villacorte *et al*., 2010b).

3.3.1.3. OTHER PARAMETERS

Numerous parameters have shown to be related to membrane fouling and their relative degree of influence cannot be decoupled in many cases when trying to determine the actual effect of a parameter of interest. For instance, there are evidences that high levels of MLSS concentrations are associated with both increases (Fane *et al*, 1981; Yamamoto *et al*., 1989) and reductions in membrane fouling (Brookes, 2006). There are also reported cases of an insignificant effect of MLSS concentration on the degree of fouling (Lesjean *et al.,*

2005). Rosenberger *et al*. (2005) tried to clarify these contradictions by noting that an increase in MLSS up to some levels of concentration (<6 g/l) reduced fouling whilst fouling propensity increased with high MLSS levels (>15 g/l); no significant effect in fouling for MLSS within a range of concentration (8 –12 g/l) was found. This could be a consequence of a change of rheology and hydrodynamics, as the effect of MLSS concentration on fouling is difficult to separate from the effect of viscosity (Drews, 2010). Some authors (Li *et al*. (2008); Meng *et al.* (2006; 2007)) reported a correlation between apparent biomass viscosity and membrane fouling, as biomass viscosity impacts flux, efficiency of dissolved oxygen (DO) mass transfer and air bubble size, with the net result of higher fouling. Regarding the level of DO in the bioreactor, this factor impacts MBR fouling by effecting the biology e.g. biofilm structure and SMP concentration. Jin *et al*. (2006) observed improved filterabilities at higher DO levels which were directly linked with higher cake porosities and larger particles measured at high DO. Dissolved oxygen must also be taken into account because EPS mineralization requires oxygen (Lu *et al*., 2001). On the other side, Yun *et al*. (2006) reported an increase of EPS concentration at higher DO levels.

Activated sludge temperature has an impact on many parameters in activated sludge. Jiang *et al.* (2005) operated an MBR at high (17-18ºC) and low (13-14ºC) conditions and concluded that a decrease in temperature has important consequences: it affects negatively nitrification and COD biodegradation rate, it reduces mean floc size and increases the release of EPS all which directly has an impact on membrane fouling. Furthermore, since high temperatures lead to stronger movement of the molecules – whereby solubility is increased and adhesive forces are decreased – a higher mass flux of SMP through the membrane could be expected at higher temperatures (Fawehinmi *et al.*, 2004). Jiang *et al.* also reported that the temperature of the biomass can affect the shear stress generated by the coarse bubble and its back transport velocity, all directly related to membrane fouling. Chiemchaisri *et al.* (1994) indicated that a change in temperature affects the filtration performance not only by affecting the viscosity but also the cake thickness and porosity. It is worth noting that several studies have concluded that the practise of normalising temperatures during the experiments to 20°C cannot totally balance these effects especially for lower temperatures (Jiang *et al*., 2005; De la Torre *et al*., 2010).

Apart from the described parameters, there are numerous other factors that may influence fouling. Van de Broeck *et al.* (2010; 2012) pointed at the bioflocculation ability as an important parameter to look at, and studied its impact on membrane fouling. They varied the bioflocculation ability by changing the ratio of monovalent over polyvalent cations in the influent of an MBR and studied changes on membrane fouling as a consequence of changes in the bioflocculation ability. Tian and Su (2012) found that sludge flocs were more stable at higher SRT after performing shear tests on them using a baffled paddle-mixing reactor. Less stable flocs obtained at low SRT were also those with higher EPS content, higher relative hydrophobicity and filamentous bacteria, all these factors generally linked with higher fouling. This fact points again at bioflocculation as a key factor for fouling.

Another parameter that has also been suspected of contributing to membrane fouling is the morphology of flocs (Li *et al*., 2008). They quantified the structure of flocs in terms of fractal dimension (D_f). A high D_f value indicated compact and dense flocs, and Li *et al.* (2008) showed that membrane fouling increased exponentially when this parameter increased.

3.3.2.FOULING MEASUREMENT

The term *fouling* expresses only an undesirable but unavoidable phenomenon but it does not express a measurable parameter. Which one is the right parameter which should be used to measure it is still to be defined. In the literature, fouling is expressed using numerous parameters like the previously mentioned SVI, TTF, fouling resistance, TMP, modified fouling index (MFI), critical flux, having each of these its pros and cons. In Table 1, a literature review about the different existing methods to determine and express fouling in MBR systems is presented.

Table 1. Review of filterability determination methods and parameters to express fouling potential (see Appendix I for extended descriptions).

	Method	Parameter measured	Units	References (selection)
Dead-end filtration	**Sludge Volume Index test**	SVI	L/mg	Kim and Nakhla (2009) Lyko *et al.* (2008)
	Time to filter test	TTF	s	Van den Broeck *et al.*(2010)
	Capillary Suction Time test	CST	s	Lyko *et al.* (2008) Sombatsompop *et al.*(2006)
	Stirred test cell	Modified Fouling Index (MFI)	s/L^2	Arabi and Nakhla (2010) Trussell, *et al.* (2007)
		Filtration resistance R	m^{-1}	Grelier *et al.* (2006)
Data observation	**System operational data observation**	Permeability	$L/(m^2 bar\ h)$	Ginzburg *et al.* (2008) Brepols *et al.* (2007)
		TMP evolution	mbar	Jiang *et al.* (2003) Wu *et al.* (2008)
		Filtration resistance R	m^{-1}	
		Specific resistance α	m/kg	Bouhabila *et al.* (2001)
		Fouling rate	mbar/min	Kim and Nakhla (2009)
Filtration test cells	**Delft Filtration Characterization Method (DFCm)**	ΔR_{20}	m^{-1}	Evenblij *et al.*(2006) Moreau *et al.* (2009)
	Berlin Filtration Method (BFM)	Critical flux	$L/(m^2 h)$	de la Torre *et al.* (2009a; 2010) (this study)
	VITO Fouling Measurement (MBR-VFM)	VFM_{rev}	%	Huyskens *et al.* (2008; 2010)
	***Ex situ* test cell**	Critical flux	$L/(m^2 h)$	Rosenberger *et al.* (2002) Schaller *et al.* (2006)
		Filtration resistance R	m^{-1}	

They have been divided into dead-end filtration, operational data observation methods and filtration test cells. They will be described in the following sections and a special section will be dedicated to the critical flux as it is a key parameter in this thesis. The methodology for each of the methods is described in Appendix I. Some parameters can also be found in the literature divided by the MLSS concentration which is helpful when trying to compare results. Table 1 presents also a selection of fouling studies references in which the parameters written in the table were applied.

3.3.2.1. DEAD-END FILTRATION

The first group of parameters shown in Table 1 was here called dead-end filtration methods, as they all are based on placing an activated sludge sample in a recipient and the parameter is obtained by applying low pressure or even by gravity-driven filtration or settling. CST, TTF and SVI are the simplest and quickest methods belonging to this group. A more complex system would include stirring and is presented in Fig. 11. A common commercial example of this is the Amicon test cell (Millipore, USA).

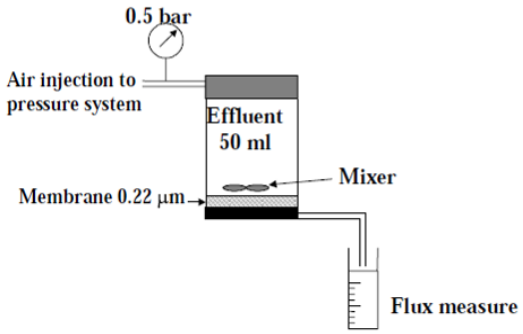

Fig. 11. Sludge filterability measurement with a stirred test cell (Grelier *et al.*, 2006).

Using this equipment, fouling can be characterised in terms of filtration resistance or modified fouling index (Schippers and Verdouw, 1980). The MFI is obtained after filtration through a 0.45 μm membrane filter and posterior plot of the ratio of filtration time and filtration volume as a function of total filtration volume. The slope of the linear region (cake filtration) of the curve obtained represents the MFI. The MFI was the basis for the UF-MFI which used an ultrafiltration membrane instead of a microfiltration membrane for the test (Boerlage *et al.,* 2004) and more recently for the NF-MFI, which uses a nanofiltration membrane (Khirani *et al.,* 2006). Nowadays, the UF-MFI at constant flux is being developed, though it needs further investigation in order to be applied (Boerlage *et al*., 2011). This will represent an important improvement for the MFI method, as it has been demonstrated that fouling mechanisms are different at constant pressure than at constant flux and that experiments at constant flux show a more complex mechanisms (Schaller *et al*., 2006).

All of them, together with TTF, SVI and CST are based on dead-end filtration, meaning that the fouling mechanisms expected from these measurements are not truly representative of those occurring during cross-flow filtration, which is the operation modus of the MBRs.

3.3.2.2. OPERATIONAL DATA OBSERVATION

The first idea when wondering how to measure fouling is to look at the MBR system operational data (basically the evolution of TMP or the resistance to filtration). Based on this approach, there exist numerous control systems which were reviewed by Ferrero *et al*., (2012). For instance Ginzburg *et al.* (2008) proposed an on-line fouling control algorithm based on the resistance in series model, which would allow the system to react with specific control actions depending on the values of the different resistances measured in the MBR unit, called the cake layer resistance (R_c) and the initial resistance (R_i). The initial resistance would include the resistance of the membrane (R_m) and the resistance caused by pore blocking (R_b) and adsorption (R_a) on the membrane. From the resistance in series equation, the total resistance (R_t) is the sum of the described singular resistances:

$$R_t=R_m+R_c+R_a+R_b \qquad [3]$$

Taking now the definition of initial resistance by Ginzburg *et al*. (2008):

$$R_t=R_c+R_i \qquad [4]$$

As they assumed that all cake layer is removed after relaxation or backwash, the total resistance at the beginning of the filtration cycle equals the initial resistance ($R_c=0$). By extracting the total resistance, the cake resistance is calculated as follows:

$$R_c= R_t-R_i \qquad [5]$$

The problem which derives from this kind of approach is naturally that it is not possible to divide this parameter into membrane resistance and pore blocking and adsorption resistance, so that in some cases the control system will not be able to distinguish between a high initial resistance caused by an activated sludge in bad conditions (in this case the action would be for instance the reduction of the flux) and a high initial resistance caused by an already fouled membrane (here the control should react applying chemical cleaning to the plant).

3.3.2.3. FILTRATION TEST CELLS

In order to disclose the influence of the activated sludge filterability and the membrane itself on fouling, it is recommended to have a device which is independent of the membrane system (filtration test cell), so that the fouling culprit (activated sludge or membrane) can be detected. Kraume *et al.* (2009) illustrated this issue with Fig. 12 (left), which shows the TMP evolution in a pilot plant.

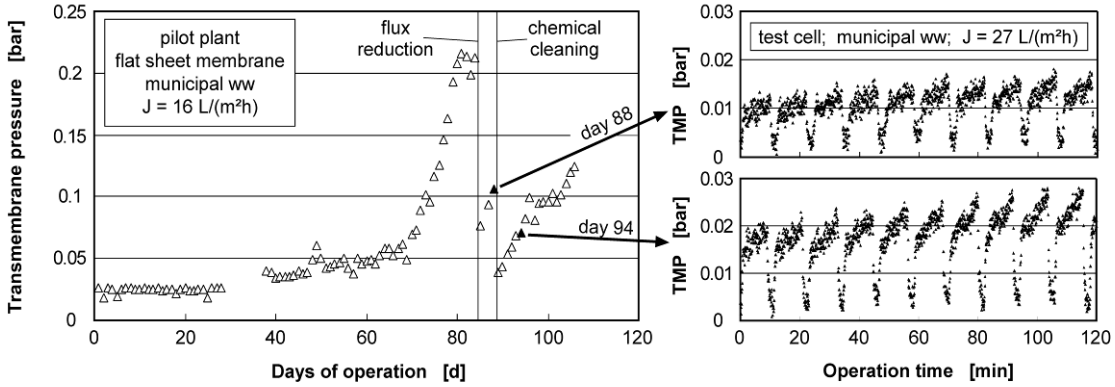

Fig. 12. Example of the filterability assessment of MBR activated sludge using a filtration test cell ($J < J_c$) (Kraume *et al.*, 2009).

After the TMP jump in the plant occurred, the flux was consequently reduced. However, the TMP rose up again in few days, and chemical cleaning was applied. Afterwards, the fouling rates were still high, which could be a consequence of an inefficient cleaning or an activated sludge with low filterability. Test cell experiments with an external test cell (Fig. 12, right) were performed before and after the chemical cleaning. Their results demonstrated that the fouling propensity of the sludge after the flux reduction was lower than afterwards. Thus, it was proven that on day 88 a fouled membrane was the reason of the high fouling rates while on day 94 the reason was probably an activated sludge with low filterability. There are sophisticated filtration test cells which were developed specifically for the filtration characterization of the sludge in MBR systems. The DFCm (Delft Filtration Characterization Method (Evenblij, 2006)), the BFM (Berlin Filtration Method) (De la Torre *et al.,* (2009a, 2010b) and the MBR-VFM (VITO Fouling Measurement) (Huyskens *et al*., 2008) are the most popular ones. The objective of the DFCm was to develop a filtration protocol under well-established hydrodynamic conditions in tubular membranes in order to obtain a standard protocol to compare the sludge filterability of the different MBR plants, independent of their configuration and operating conditions. The filterability of the mixed liquor is expressed as a ΔR_{20} value, which represents the increase in additional membrane filtration resistance after extraction of 20 L/m² of permeate. Normally a ΔR_{20} value below $0.2 \cdot 10^{12}$ m^{-1} is considered typical for good filterable mixed liquors, whereas ΔR_{20} values above $1 \cdot 10^{12}$ m^{-1} are characteristic of an

activated sludge with bad filterability. One of the disadvantages of the method is that it is *ex situ* (external to the MBR plant), which involves transport and storage of the sludge into a tank, where the measurement take place. The influence of storage time was already highlighted by Kraume et al. (2009), who showed that activated sludge filterability deteriorates after a few hours of storage. However, in the case of the DFCm, the experiments are normally performed close to the sampling point avoiding severe activated sludge deterioration due to transport. An important drawback of this method is that the operating conditions are far from those generally encountered in an MBR system, as the idea is to accelerate fouling by working at extreme conditions (high flux). The idea of an *ex situ* test cell has been also applied by other authors (Rosenberger et al. 2002, Schaller et al., 2006) but they determined filterability using critical flux tests and used a flat membrane which was replaced after each experiment.

In contrast to the DFCm, the BFM and MBR-VFM use an *in situ* aerated test cell, which means that the test cell is directly submerged in the sludge tank. This way, they eliminate problems like sludge transport and storage or different fluid dynamic conditions typically encountered in common filterability measurements (Kraume *et al*., 2009).

In the case of the MBR-VFM, the determination of the filtration resistance is carried out at constant pressure using a PVDF tubular membrane (X-Flow, the Netherlands). The filtration protocol consists in conditioning, filtration at low aeration to promote reversible fouling, relaxation and posterior filtration at high aeration. These data are introduced in an advanced control system (ACS) as an input, together with the temperature and the flux data. As an output, the ACS gives an aeration value for the actual filtration conditions. Using this control system during 1.5 year, Huyskens *et al.* (2010) reported a reduction of 22% in the aeration needed in their plant. Nevertheless, the ACS system was not able to avoid the severe fouling experienced due to the rapid change in temperature in winter. This is expected to be solved via a more precise tuning of the control system. A scheme of the MBR-VFM is given in Fig. 13.

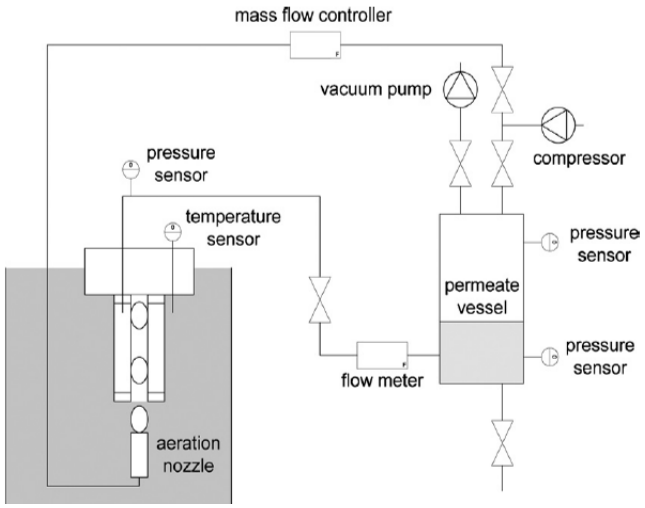

Fig. 13. Schematic overview of the MBR-VFM set-up (Huyskens *et al*., 2008).

Contrary to the MBR-VFM, the BFM uses constant flux, which is the common operating mode in the real MBR plants. The filterability of the activated sludge is expressed by its J_c value. Operation and design of the filtration BFM test cell are as similar as possible to those of a real plant and is further described in de la Torre *et al.* (2009a; 2010a).
Both MBR-VFM and BFM are oriented to the implementation of their fouling measurement in the control of the plant and they provide additional information about the irreversibility of fouling. Apart from the differences in apparatus configuration, both MBR-VFM and DFCm are based on the evolution of the fouling rate in time, whereas the BFM performs flux-stepping experiments in order to determine the critical flux performed under normalised conditions. While the BFM perform flux plateaus resulting in increasing TMP values, the MBR-VFM operates at constant pressure plateaus results in decreasing flux values.

3.3.2.4. CRITICAL FLUX

The critical flux concept has been widely used in the determination of fouling propensity of solutions since its introduction by Field *et al.* in 1995. They defined two types of critical flux, namely the strong form and the weak form. The strong form of the critical flux equals pure water flux derived under the same conditions as those obtained with the feed solution. It is noted as the flux at which the TMP starts to deviate from the pure water line. In the weak form, the critical flux is the subcritical flux established and maintained during the start-up of filtration but not necessarily corresponds to clean water flux. Here the flux-TMP relationship is below the pure water line and the critical flux (weak form) is the point at which this line becomes non-linear. Fig. 14 shows the differences between both the strong and weak forms of the critical flux.

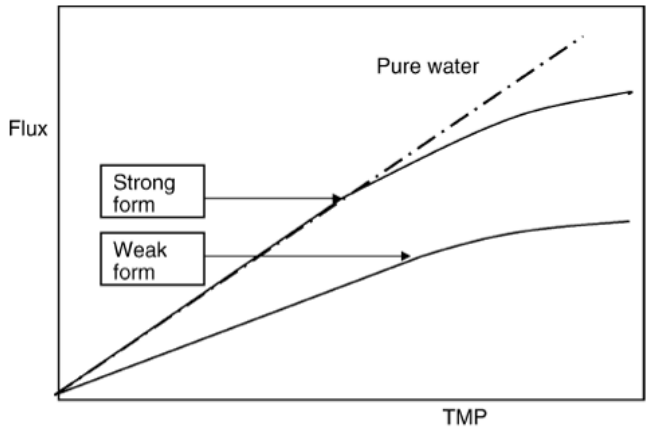

Fig. 14. Strong and weak form of the critical flux defined by Field *et al.* (1995).

Various studies (Cho *et al*., 2002; Ognier *et al*., 2004; Guglielmi *et al*., 2007a) have shown that a two-stage phenomenon in fouling (gradual and stable fouling and rapid fouling) is apparent in MBRs. Brookes *et al.* (2006), in their study using different MLSS concentrations also showed this phenomenon in fouling at fluxes below 10 L/(m²h), but

only at low MLSS concentrations (<6 g/L). At a flux of 10 L/(m²h), no stable low fouling period was exhibited, but rather a linear fouling from the beginning of the experiment followed by a rapid fouling after 2 days of operation. Operation at the lowest flux of 2 L/m²h showed stable operation for up to 10 days, albeit with some fouling taking place (dTMP/dt = $7 \cdot 10^{-4}$ mbar/min) confirming subcritical fouling. This has led to suggestions that there is a transition period between constant and non-constant permeability and hence reversible and non-reversible fouling (Guglielmi *et al*., 2007b).

The concept of flux sustainability is a more realistic idea and is defined as the flux for which the TMP increases gradually at an acceptable rate such fouling is minimized to avoid frequent cleaning (Bacchin *et al*., 2006). This concept corresponds to a flux at which continuous operation is maintained with slow and gradual fouling taking place over a given period of time without a sudden increase in transmembrane pressure (rapid fouling). The application of the sustainable flux concept attempts to distinguish between low and high fouling rates, even though the value may be somehow subjective and dependent on duration of operation. As noted by Ognier *et al.* (2004), the duration of the operation is of importance in assessing the sustainability of a flux value, as a small fouling rate may be acceptable for shorter operational time but becomes unsustainable at longer operation. It is also worth noting that another study from Brookes *et al.* (2006) could not corroborate the sustainable flux phenomenon.

As already mentioned, there exists a lack of standardization in the MBR technology, and this is also present in the application of the critical flux concept. There are numerous protocols for its determination and the absolute value of the critical flux is dependent on the method employed for its determination (Judd, 2006). Therefore it is important to analyse which are the different protocols available and what is the information that can be expected from a critical flux experiment.

Typically used are the flux-stepping methods for the determination of this parameter. They consist in increasing the flux gradually and registering the corresponding TMP evolution as in Fig. 15, which presents an example of critical flux determination for an agarose solution.

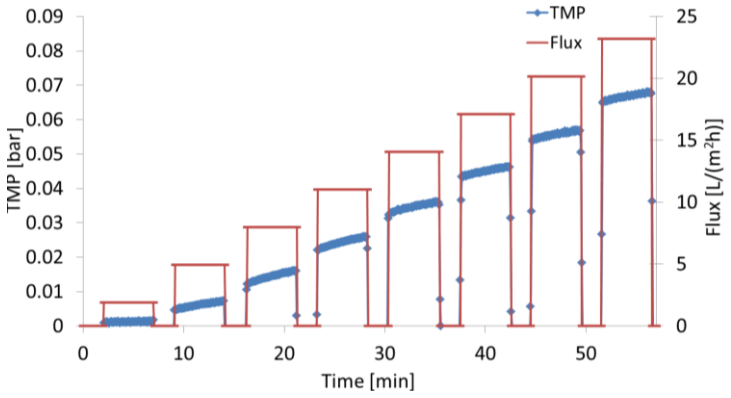

Fig. 15. Flux-stepping protocol for critical flux determination (De la Torre *et al*., 2009b).

The critical flux can be detected either visually or by establishing a concrete criterion. For example, it can be agreed that J_c is achieved when the fouling rate reaches 0.1 mbar/min. Several J_c determination criteria were compared by Le-Clech *et al.* (2003).

Because of the lack of a standard protocol for the performance of these flux-stepping experiments, different protocols have been proposed by numerous authors. Several authors (Espinasse *et al*., 2002; Le-Clech *et al*., 2003) used protocols which also included flux-down stepping and giving therefore information about the irreversibility of the deposition of the foulants on the membrane surface by looking at the hysteresis of the TMP evolution. In own studies (De la Torre *et al*., 2010b) three protocols for the determination of the critical flux were compared, consisting of modified flux-stepping methods:

Classical protocol: Described in (Le-Clech et al., 2003) and represented in Fig. 16. (left). The flux is increased stepwise and decreased until the initial value is reached.

Filtration/Relaxation protocol: It is basically the *classical protocol* with relaxation between filtration steps (Fig. 16. II). The objective is to make the filtration regime more similar to the plant operation regime, in which relaxation commonly takes place and the membrane virtually recovers from all reversible fouling that accumulated during filtration.

Pre-step protocol: A modification of the *Filtration/Relaxation protocol* is introduced here by filtering at a constant low value (5-10 L/(m²h)) for two minutes before every filtration step (Fig. 16. III). The objective is that, by looking at the evolution of the transmembrane pressure (TMP) in this pre-filtration step, a special parameter can be obtained which can give information about the irreversible fouling, i.e. the fouling remaining after the relaxation step.

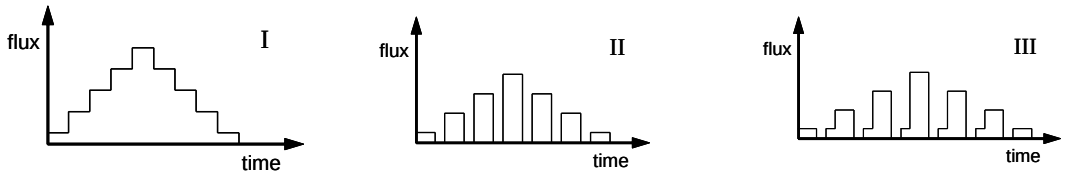

Fig. 16. I. *Classical* protocol, II. *Filtration/Relaxation* protocol, III. *Pre-step* protocol (De la Torre *et al*., 2009a).

The results from this comparison are shown in Fig. 17 and Fig. 18. As expected, the results from the filtration/relaxation protocol and pre-step protocol were quite similar, and differed from the classical protocol (protocol I) in terms of average TMP in the filtration steps. When using the classical protocol (protocol I), an accumulation of the cake on the membrane occurs along the cycle after the critical flux is reached and a hysteresis phenomenon always takes place. The membrane history influences the measurement using protocol I because of the lack of a relaxation step, so that the results are very dependent of the flux-step height and duration. With the other two protocols, the result of applying relaxation between steps is that the membrane starts the following filtration step without being significantly influenced by the membrane history so that the pressure by increasing the flux must be the same as the pressure obtained by going down in the flux for the same flux (no hysteresis effect).

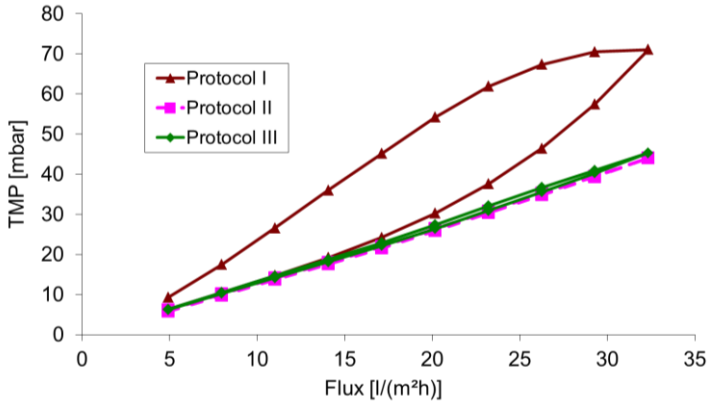

Fig. 17. TMP (average of each flux step) versus flux in the protocol comparison (De la Torre *et al.*, 2009a).

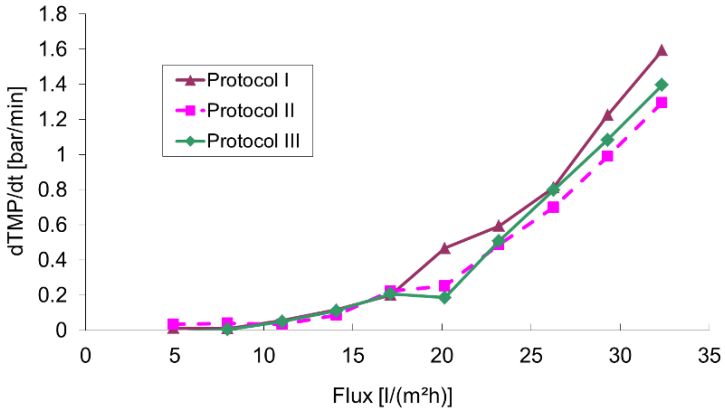

Fig. 18. Fouling rates in the protocol comparison (De la Torre *et al.*, 2009).

It is remarkable that in terms of fouling rate, all protocols exhibited very similar results. Furthermore, the J_c values obtained with the three protocols gave the same values with a maximal difference of one flux step for the selected criteria (dTMP/dt<0.2 mbar/min). Due to the membrane history, we could have expected a higher fouling rate for protocol I, at least for fluxes above the critical flux (due to higher TMP after at least 30 min of continuous filtration without relaxation). On the other hand, a classification effect might have taken place during the protocols with relaxation, because the increment of flux is quite high in the last steps, going up to 30 L/(m²h). This effect was reported for solutions of colloidal silica (Chen *et al.*, 1997), where it was shown that a great flux increase at once led to a higher dTMP/dt value due to a faster developed and therefore more chaotic fouling layer than the obtained by a slowly increasing of the flux. The contrary effect was found from other authors (Wu *et al.*, 2008). These two effects (classification effects on the one hand and relaxation neglecting the membrane history) might be both negligible, or might have cancelled each other out and the differences between protocols from the results of this study are therefore not significant. In some cases, some hysteresis can be observed even with protocols II (filtration/relaxation) and protocol III (pre-step protocol) due to remaining fouling in the membrane which could

not be eliminated with the relaxation, as it was shown in De la Torre *et al*. (2009a) for an activated sludge showing poor filterability. This remaining fouling causing the hysteresis in the curve was called irreversible fouling.

Protocol III was selected as the most interesting protocol of the three protocols compared as, due to the short pre-step at low flux, it offers the following specific advantages: it enables a quicker stabilisation of the pressure value when applying the higher flux step, therefore provides cleaner data, but which is more important is that it provides a direct measure of irreversible fouling during the pre-step, straight after the relaxation phase.

Van der Marel *et al*. (2009) obtained the value of the *critical flux for irreversibility*, using a combination of protocols II and III resulting in a protocol with flux-down stepping and partial relaxation (filtration at low J), which is presented in Fig. 19.

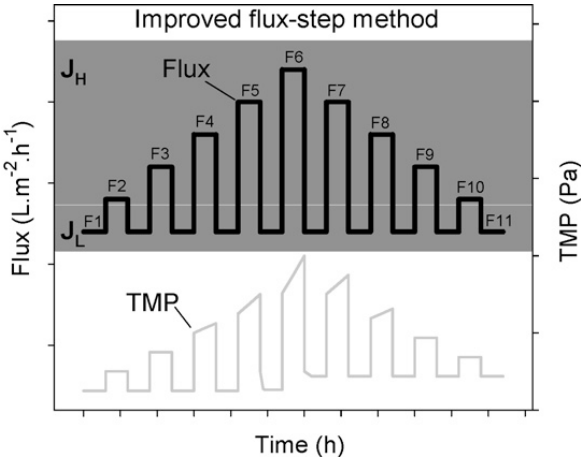

Fig. 19. Critical flux determination protocol by van der Marel *et al*., (2009).

By working with municipal wastewater and an aerated PVDF flat-sheet membrane of 0.1 µm, they found that the cake formed by filtering activated sludge was removable up to a flux of 100 L/(m²h). The critical flux for irreversibility was therefore larger than 100 L/(m²h). The introduction of the partial relaxation reduces the influence of fouling history so that there is almost no fouling rate hysteresis during the flux-down stepping.

More recently, Navaratna *et al*. (2011) introduced the *prolonged flux-step method*, in which the flux step duration is 7 days and the flux step height is 1.2-1.5 L/(m²h). They operate with intermittent permeate suction (12 min "on" and 3 min "off") and obtained more realistic critical flux values than those obtained with short flux-step tests. Nevertheless, the duration of the test is an important drawback of the protocol and maintaining uniform sludge conditions throughout the test presented an important difficulty in the performance of the test.

The applicability of short-term test like flux-step experiments to evaluate long-term fouling of MBR systems has been studied by several authors. In their long-term trials, Guglielmi *et al*. (2007b) confirmed the reliability of the results from the short-terms tests performed following their flux-stepping protocol. However, Le-Clech *et al.* (2003)

concluded that flux-step determination of the critical flux cannot be used to predict long-term TMP behaviour in real MBR systems, but nonetheless provides useful data on comparative fouling propensity. Recent studies from Saroj *et al.* (2008) obtained a model for sub-critical flux operation and succeed in predicting the time at which TMP jump occurred in an MBR treating municipal wastewater.

4. STUDIES WITHIN THIS THESIS: THE QUEST FOR A UNIVERSAL FOULING INDICATOR

4.1. PRELIMINARY STUDIES

As already mentioned, preliminary studies were performed in order to validate the novel methods applied within this work: the BFM and the TEP. On the one hand, the BFM was compared with existing filterability determination methods. On the other hand, filterability studies with model polysaccharide solutions were performed in order to get a better understanding of the significance of the parameter TEP and the fouling importance of polysaccharides.

4.1.1. PRELIMINARY STUDY I: VALIDATION OF THE *IN SITU* BFM TEST CELL

Measurements in parallel with other two methods for MBR filtration characterization were performed in order to validate the developed *in situ* BFM. A detailed description of these validation experiments can be found in (De la Torre *et al*., 2009a). The compared methods were the Delft Filtration Characterization Method (DFCm) and the critical flux determination using an *ex situ* side-stream filtration test cell design and constructed at the Technical University of Berlin. The mixed liquor filterability of four different MBR units was characterised with the three methods, which were already presented in the background section and in 3.3.2.3 and are summed up in Table 2. The MBR units are here called MBR1, MBR2, MBR3 and MBR4 and are briefly described in section 4.2.1. Details about their equipment and operation can be found in Evenblij *et al*. (2003; 2006) for the DFCm, in De la Torre *et al*. (2009a; 2010b) for the BFM and in Rosenberger and Kraume (2002) for the *ex situ* test cell. A basic scheme of the three test cells can be seen Fig. 20-22.

Table 2. Description of the three filterability characterization methods compared.

	Membrane cleaning	Measured parameter	Membrane material	Pore size	Membrane configuration	Membrane scouring	Sludge transportation
BFM	When water Pe decreases 10%	J_c	PES	150 kD	Flat sheet	Yes	No
DFCm	After each experiment	ΔR_{20}	PVDF	0.03 μm	Tubular	No	Yes
Ex situ test cell	No (new membrane for each test)	J_c	PVDF	0.2 μm	Flat sheet	Yes	Yes

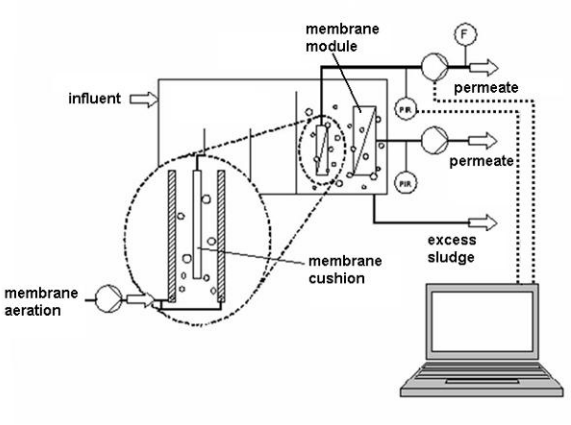

Fig. 20. Scheme of the BFM test cell equipment (*in situ* test cell) (De la Torre *et al*., 200a; 2010b)

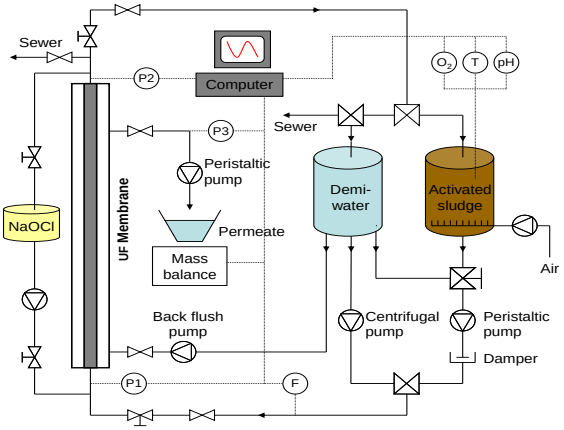

Fig. 21. Filtration Characterisation Installation (Evenblij *et al*., 2006).

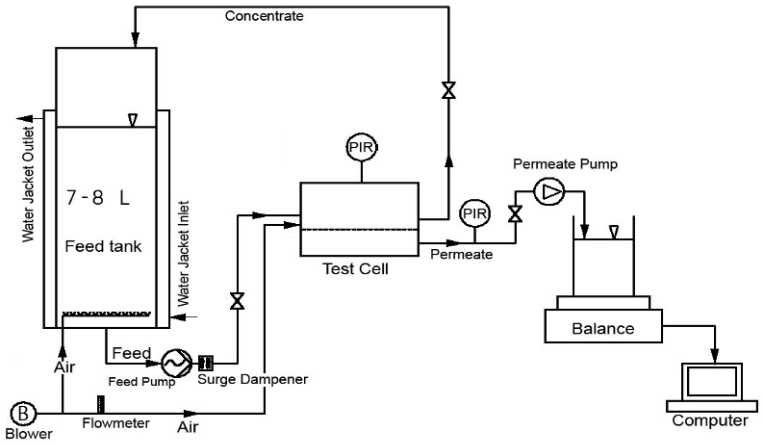

Fig. 22. *Ex situ* test cell installation diagram (Rosenberger *et al*., 2002).

Fig. 23 shows the results of the comparison of the BFM and the DFCm. As presented in Equation [1], filtration resistance and flux are inversely proportional and therefore the $1/J_c$ was represented versus ΔR_{20}. It can be seen that there were some differences in the results which were related to different configurations, operating conditions and membrane materials. However, the critical flux obtained with the BFM and the filtration resistance measured with the DFCm are inversely proportional with a correlation coefficient of 0.77 for three of the biological sludges (MLSS range 7-16 g/L). The correlation was not valid any more for MBR4, which activated sludge showed a good filterability with the DFCm but it presented a low critical flux with the BFM. This was attributed to the unstable operation during the start-up phase of the unit and the adaptation phase after seeding as well as to the low concentration of suspended solids of the plant (4 g/L MLSS): BFM and DFCm might not be comparable under these conditions.

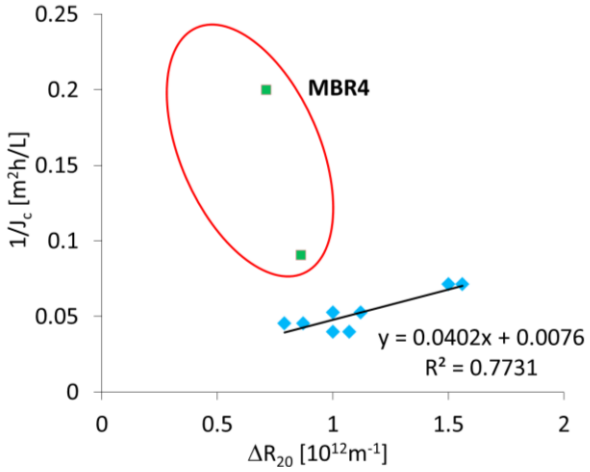

Fig. 23. Results of J_c and ΔR_{20} values obtained in the comparison campaign (De la Torre *et al.*, 2009a).

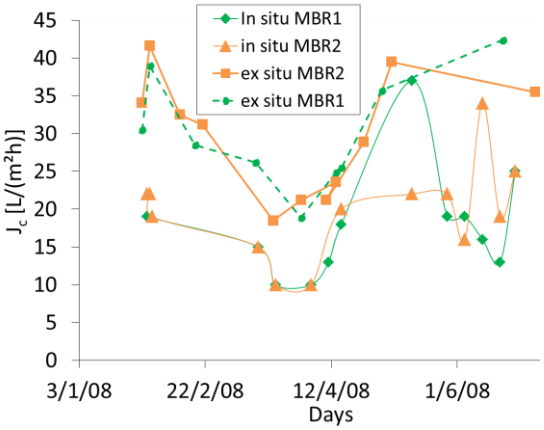

Fig. 24. Results of the BFM and the *ex situ* filtration test cell during the regular monitoring of the plants (De la Torre *et al.*, 2009a).

Fig. 24 reflects the comparison performed between the *in situ* BFM and *ex situ* test cell during more than six months in MBR1 and MBR2. A direct comparison is difficult because the measurements were done on different days but it can be noticed that the same trend was followed by both of them, although the results are not strictly equivalent probably due to the differences in the operating conditions of the test cells. When looking at the absolute J_c values, higher values are found with the *ex situ* test cell than when using the BFM. This may be attributed to the lower pore size of the membrane in the case of the BFM, although some authors have found lower fouling rates in MF membranes than in UF membranes caused by pore clogging of the MF membranes by large particles, and protection of the UF membrane by the large particles acting as a secondary membrane (Choi *et al.*, 2005). Another reason might be that the criterion used to determine the critical flux in the case of the *in situ* test cell results in more conservative J_c values. In the *ex situ* test cell, the sludge is pumped at high cross-flow velocities along the membrane, which causes high shear forces so that the dTMP/dt value selected for the determination of the critical flux (dTMP/dt<1 mbar/min) is much higher than in the BFM (dTMP/dt<0.2 mbar/min), in which the sludge circulates only with the help of air scouring.

From these results, the validity of the BFM for the determination of the filterability of sludge was demonstrated and this tool was selected for the evaluation of fouling propensity of sludge in the quest for a universal fouling indicator.

4.1.2.PRELIMINARY STUDY II: TEP IN MODEL SOLUTIONS

As alcian blue only binds to carboxyl (-COO-) and half-ester sulfate (OSO3-) reactive groups of acidic polysaccharides, the interest in TEP in fouling investigations depends on the fouling propensity of this kind of polysaccharides. The interest of measuring TEP in MBR system will be only justified if it is demonstrated that indeed different polysaccharides present different fouling propensity, and especially if those showing higher TEP values present higher fouling propensity. As it was previously mentioned, one of the reasons of the controversial results when dealing with polysaccharides and fouling might be the wide variety of carbohydrates present in the nature that show very different properties and may also consequently show different fouling propensity. Numerous studies have been conducted for the study of polysaccharide fouling using model solutions, but they were often conducted using only one compound (mostly sodium alginate) as a model polysaccharide (Ye *et al*., 2006; Katsoufidou *et al*., 2008; Jermann *et al*., 2007). In addition, in most of these articles, the experiments were performed using dead-end filtration whereas membrane bioreactor processes operate under *quasi* cross-flow conditions due to air scouring. As it is well known, the fouling mechanisms that occur in dead-end filtration are different from those encountered during cross-flow filtration (Schaller *et al*., 2006). To elucidate contributing factors to varying fouling propensity of polysaccharides, the influence of the characteristics of the polysaccharides on membrane fouling was studied within this work by comparing the filterability of different solutions of model polysaccharides using the Berlin Filtration Method. Critical flux measurements were performed with solutions of eight different substances with different functional groups. Four compounds with carboxylic groups were selected (xanthan gum, alginate, carboxymethylcellulose (CMC) and pectin), two with half-ester sulfated groups (heparin and carrageenan) and two neutral polysaccharides (agarose and starch). As it was described in the background section, only PS with carboxylic or half-ester sulfated groups are bound by alcian blue. The reason of selecting also neutral polysaccharides for the experiment was to evaluate if PS belonging to TEP are the only PS causing fouling. Solutions of 20 mg/L of all PS were prepared and pH and conductivity were adjusted at 7.5 and 800 µS/cm respectively. In the resulting PS solutions, the concentrations of total polysaccharides were measured and expressed as mg of glucose equivalent per liter. TEP concentrations were also measured in the eight solutions and the results were expressed in mg xanthan equivalent per liter. These and other properties like gelling properties, viscosity, functional group and molecular weight were studied in the model solutions in order to find any possible relationship of these parameters and the fouling occurrence in terms of critical flux. The experimental procedure is presented briefly in Table 3 and more in detail in De la Torre *et al*. (2009b). Basic molecular properties of the studied polysaccharides are presented in Table 4.

Table 3. Experimental conditions of the filtration tests.

Model solutions	pH	7.5
	Ionic strength	800 µS/cm (adjusted with NaCl)
	Concentration	20 mg/L
Filtration parameters	Equipment	BFM test cell
	Filterability determination	Critical flux experiments
Analytical methods	PS determination	Dubois *et al*. (1956)
	TEP determination	De la Torre *et al*. (2008)

Table 4. **Basic properties of the investigated polysaccharides.**

Polysaccharide	Supplier	Functional group	Medium molecular weight (MW) polymer [kD]	MW monomer [g/mol]	Gelling properties
Xanthan	Rhodia	-$COOH^-$	500-500000	934	Mainly considered as non-gelling
Alginate	Carl Roth		1-154	175	Forms gels with Ca^{2+}
CMC	Carl Roth		250-50000	189	Non-gelling at the studied conditions
Pectin	Natura		30-100	158	Gel with high concentrations of cosolutes (e.g. sugar) and pH < 3.4
Heparin	Carl Roth	-OSO^{3-}, -$NHSO^{3-}$ and -$COOH^-$	3-50	195	Non-gelling
Carrageenan	Sigma Aldrich	-OSO^{3-}	20-1000	Not applicable	It forms gels with Ca^{2+}. Without Ca^{2+}, considerable thickening occurs
Agarose	Carl Roth	-	170	Not applicable	It forms gels after cooling
Starch	Merck	-	130	162	It forms cohesive and clear gels

4.1.2.1. J_C OF MODEL POLYSACCHARIDES SOLUTIONS

The results from the flux stepping experiments can be seen in Fig. 25, where the average TMP of each flux step is represented against the J_c. In most curves, the expected convex trend typical for critical flux measurements could not be observed, which was attributed to the relaxation breaks. It is noticeable that the filtration resistances for carrageenan and agarose were significantly higher than for the other polysaccharides.

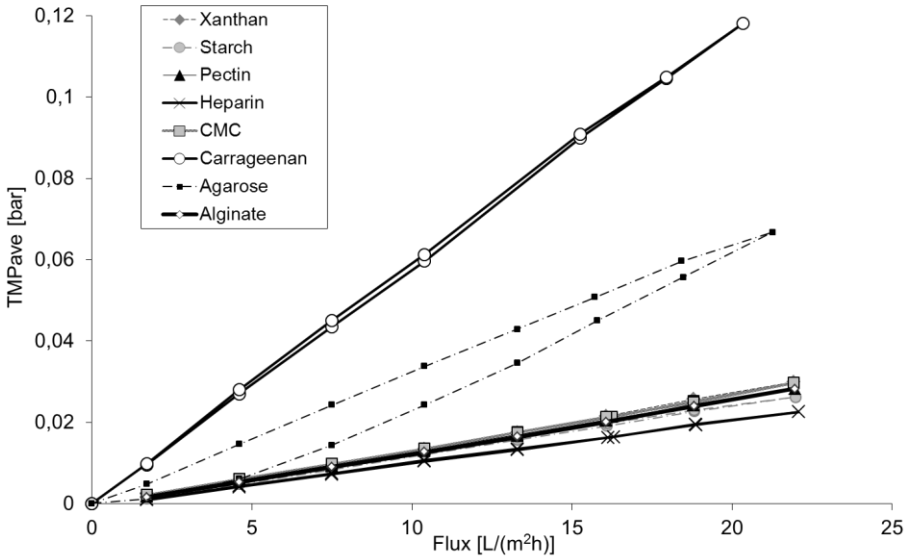

Fig. 25. TMP average and flux during the experiments (De la Torre *et al.*, 2009b).

Further differences in the fouling properties of the polysaccharides can be seen by looking at the TMP evolution when filtering the solutions of pectin and agarose (Fig. 26a). Taking the TMP and flux evolution (Fig. 26b), no significant fouling was detected by filtering the pectin solution; the evolution of the TMP with the flux presented the same pattern by both increasing and decreasing the flux. On the other hand, the severe fouling produced by agarose did not allow the TMP to recover by reducing the flux, as can be seen from Fig. 26b. This was related to the phenomenon of mechanically irreversible fouling. This hysteresis phenomenon was observed especially in those experiments which were run much beyond the critical flux values (those with low J_c: carrageenan, agarose), and demonstrated the fact that for these substances, the 2 min relaxation steps do not allow, under the conditions of the trials, to recover the loss of permeability due to cake building during the filtration.

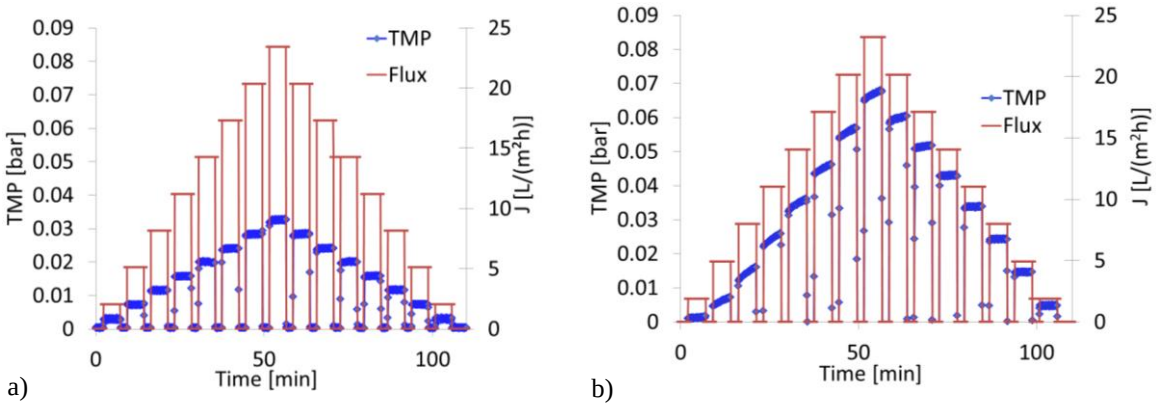

Fig. 26. Critical flux measurement of a 20 mg/L pectin solution (a) and a 20 mg/L agarose solution (b). TMP and flux evolution. (de la Torre *et al.*, 2009b).

4.1.2.2. CARBOHYDRATE AND TEP CONCENTRATION

By looking at the studied properties of the polysaccharides, no direct relationship could be observed between these and the filterability behaviour in terms of critical flux value or hysteresis of their curves. As it can be seen in Fig. 27, different filtration behaviour was found for the different polysaccharides (critical flux values varied between 3 and 21 L/(m²h)), but that could not be strictly related neither to the measured amount of PS following the conventional method (phenol-sulfuric method (Dubois *et al.*, 1956)) nor to the TEP concentrations of the solutions. TEP concentrations of 0 mg/L xanthan equivalent were found for agarose and starch as expected, being neutral polysaccharides not detected by the analysis with alcian blue. This fact questioned the relevance of the concentration of TEP as a fouling indicator because, as it was seen with agarose, neutral sugars can also contribute significantly to the fouling phenomenon with the investigated membranes (very low J_c).

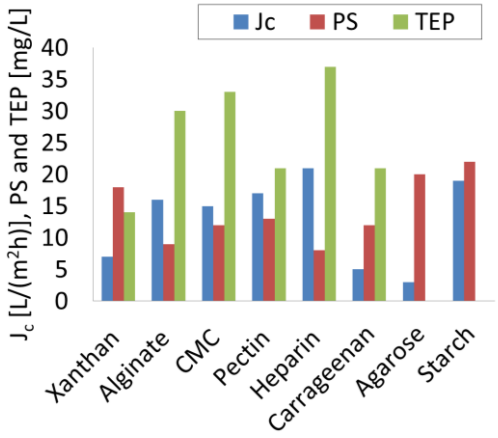

Fig. 27. J_c, TEP and PS concentrations of the model solutions (De la Torre *et al.*, 2009b).

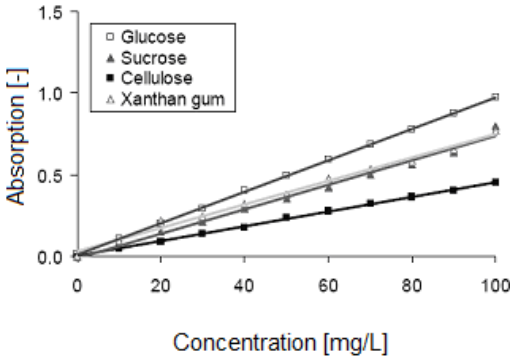

Fig. 28. Calibration curves for different sugars using the phenol-sulfuric method. (Mehrez *et al.*, 2007).

Although the model solutions were all prepared with 20 mg/L polymer mass, the global PS method resulted in very different concentrations. The reason for this discrepancy is that, using the phenol-sulfuric method, each polysaccharide yields a different absorbance after reacting with the sulfuric acid for the same concentration of 20 mg/L.

When these absorbance values are then referred to the calibration curve of glucose, values from 8 to 22 mg/L were obtained. This is an inherent consequence of the calibration with a standard, as it reflects the problem of measuring total concentrations of sugar with this method, which was developed only for pure sugar solutions calibrated with the same sugar which is being measured. The same situation occurs with the TEP concentrations. Therefore, it seems reasonable that no relationship between filterability and these concentrations could be found. Nevertheless, this is not in contradiction to the hypothesis of TEP being the main PS causing fouling in MBR. Even though there are PS that may cause severe fouling (like agarose), these might not be present in MBR system and those causing fouling might be those belonging to TEP. In other words, there are different groups of sticky PS, and TEP could still be the group of sticky PS which is mainly present in MBR. Whether this hypothesis is valid or not will be evaluated in the monitoring campaign section (chapter 4.2).

4.1.2.3. MOLECULAR SIZE

In
Fig. 29, the molecular weight of the different PS is represented against the critical flux values obtained. The average, maximum and minimum MW values were taken from diverse literature sources and, as this parameter varies considerably depending on manufacturing procedure, supplier, raw material, etc. in biopolymers, the range found in the literature is considerably wide. However, it can be appreciated that the MW of the polymers does not explain the critical flux values measured. A possible relationship between the critical flux value and the molecular weight of heparin may exist as this polysaccharide showed a very high filterability, and it has the smallest molecular size with approximately 15 kD, which is much lower than the MW found in the literature for the other polysaccharides. This low value for the MW is also much lower than the MWCO of the membrane (150 kD), which probably permitted the polysaccharide molecules to pass through the membrane without disturbing filterability.

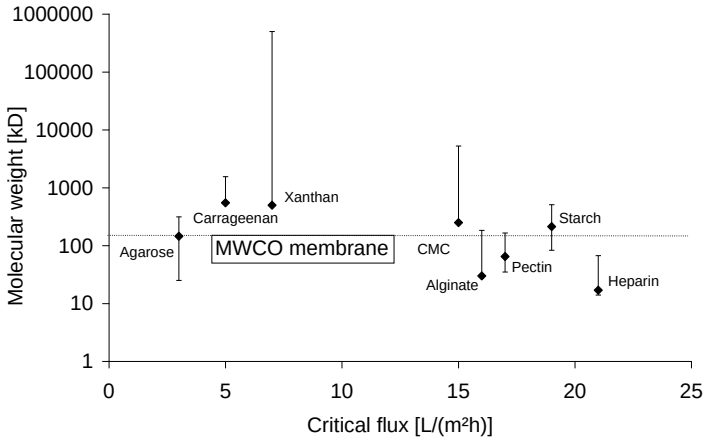

Fig. 29. MW and critical flux values. Error bars indicate max. and min. values, symbols average (De la Torre et al., 2009b).

4.1.2.4. CHARGE DENSITY

The charge density was estimated by calculating the number of electric charges in the monomers divided by the molecular weight of the monomers. As this was represented against critical flux, a clear trend indicating higher critical flux at higher charge density of the polymers was found, especially by the PS containing carboxylic groups. Sulfated groups seem not to influence filterability as much as carboxylic groups, as it can be seen in Fig. 30. This suggests a charge repulsion effect between the hydrophilic PES membrane (used in the BFM) and the negatively charged polysaccharides, leading to higher rejection and less interaction between molecules and less adsorption. Lower flux decline and adsorption during the filtration of natural organic matter with hydrophilic PES membranes at higher negative charge due to carboxylic groups (higher pH) was already reported in the literature (Amy *et al.*, 2001).

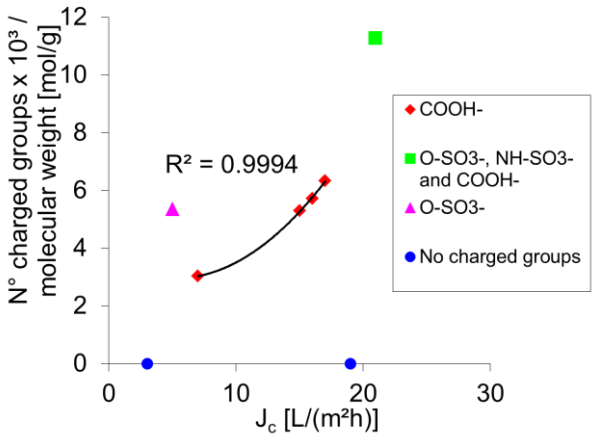

Fig. 30. Influence of the number of charged groups per monomer divided by MW in the critical flux values (De la Torre *et al.*, 2009b).

4.1.2.5. CONCLUSIONS TEP IN MODEL SOLUTIONS

By looking at the different substances tested, each of them may have a different reason for their J_c value and a clear correlation of this parameter and parameters like viscosity, MW, charge density, PS or TEP concentration could not be demonstrated here. However, as it was previously discussed, this does not necessarily mean that these parameters are not relevant for fouling, as the relative influences of all parameters cannot be distinguished and the influence of a single parameter can thus become diffuse. The gelling capacity of the substances did not seem to be the most significant characteristic for fouling, showing starch and agarose (those substances which form gels under the studied conditions) the highest and the lowest critical flux values, respectively, as can be seen in Fig. 27. This might be attributed to a different gel

structure which consequently caused different fouling. The high filterability of heparin was explained by its low molecular weight, being the polysaccharide able to pass the membrane without affecting the TMP value. The medium fouling propensity of compounds like CMC, xanthan gum (XG) or alginate can be related to their already known "stickiness" and their acidic nature, which makes them more likely to interact with the hydrophilic membrane than a neutral polysaccharide like starch, which showed the highest J_c value together with heparin. The severe fouling encountered by filtering the carrageenan solution could not be explained by looking at any of the studied parameters. The main conclusions described in this section are summed up in Table 5.

Table 5. Sum up of the model solutions study.

Characteristic	Influence on Jc	PS showing influence
PS content [mg glucose equ./L]	Not shown	-
TEP content [mg XG equ./L]	Not shown	-
Molecular weight	↓ MW ↑J_c	Heparin
Charge density	↑Charge density ↑J_c	XG, CMC, Alginate, Heparin, Pectin
Gelling capacity	↑Gelling capacity ↓J_c	Agarose

The significant differences encountered in the fouling propensities of the polysaccharides and the lack of a relationship with the measured parameters question the usefulness of the employed analysis methods and confirm that the quality of the polysaccharides can be more important than quantity when dealing with fouling issues. Even the same polysaccharide can behave differently depending on the source and/or the industrial process used to extract and purify those (Rinaudo *et al*., 2004) because the chemical structure of these polysaccharides varies. It can be concluded that, when working with model PS, their selection must be very careful and the representativeness of a model solution is questionable. In the last years, articles investigating the filterability of different mixtures of polysaccharides and calcium ions as well as humic substances in different pH conditions have multiplied, which shows that it has been noticed that we are dealing with a complex phenomenon which cannot be simplified with the use of a model solution of a single compound. Also the membrane material plays an important role, as well as the pore size and hydrophobic/hydrophilic character; so that the conclusions obtained for one membrane material cannot be extrapolated for the rest of them.

The incapacity of the phenol-sulfuric method for the quantification of PS mixtures revealed that findings based on this lump parameter are questionable. The results stress the difficulty of finding a global fouling indicator for polysaccharides and question the representativeness of the use of model polysaccharides in fouling investigations.

4.2. MONITORING CAMPAIGN

Seventeen parameters were monitored during ten months on a weekly basis in the mixed liquor and permeate of four MBR units. Parallel to this, the critical flux of the activated sludge of the units was determined using the BFM. The relationship of the measured parameters and the critical flux was evaluated with the statistical software SPSS using univariate and multivariate analysis in order to find the main parameters influencing membrane fouling in MBR systems.

4.2.1. MBR UNITS AND MONITORED PARAMETERS

The main characteristics of the investigated MBR units during this study are presented in Table 6. MBR1 and MBR2 worked in parallel as part of a pilot plant consisting of an anoxic chamber followed by an aerobic chamber where the membranes were submerged. MBR3 was a demonstration plant designed for enhanced biological nutrient removal. A second unit (MBR4) was installed in January 2008 parallel to the MBR3 unit to deal with part of the MBR3 influent and perform COD removal and nitrification. MBR1 and MBR2 were fed with municipal wastewater and in MBR2 a flocculant for permeability enhancement was added periodically. MBR3 and MBR4 treated domestic wastewater. Further details of MBR1 and MBR2 can be found in Iversen *et al*. (2009) and details about MBR3 and MBR4 in Vocks *et al*. (2005) and Stüber *et al*. (2009).

Table 6. **Operating conditions of the four investigated MBR units.**

	SRT	TS*	COD supernatant	COD influent	Activated sludge temperature
	(d)	(g/L)	(mg/L)	(mg/L)	(°C)
MBR1	12	4-13	20-125	120-1600	16-28
MBR2	12	5-12	30-150	120-1600	16-26
MBR3	25	13-22	90-850	750-2500	10-26
MBR4	35**	5-13	48-440	750-2500	10-23

*Total solids of mixed liquor taken from the membrane tank. For the treated influent, TS=MLSS+1 g/L approximately.

**from April 2008. Before that, no sludge withdrawal (SRT>200 d).

Some parameters were measured in different fractions of the activated sludge, which were obtained after fractionation using series of microfiltration filters with nominal pore sizes of 50 µm, 10 µm, 2 µm and 0.2 µm. Details on fractionation and analytical procedures are described in De la Torre *et al*. (2010a).

For the evaluation of the results, some parameters were calculated like the colloidal fraction and the rejection of the PS, PR, TEP and biopolymers. The colloidal fraction for these parameters obtained by extracting the value measured in the permeate from the

total value in the sludge filtrate. This way, the colloidal fraction comprised the fraction which ranged from the pore size of the membrane to the pore size of the paper filter and represent those colloids which are retained by the membrane. The rejection was calculated by dividing the colloidal fraction by the total value.

Besides, the CST and TTF were normalized by dividing by the total solids concentration. The calculated parameters as well as the samples used for the measurement and the period in which the parameters were monitored are presented in Appendix II. An abbreviated list is presented below (Table 7).

Table 7. Monitored parameters.

Parameter	Acronym
Biopolymers	Biopol
Capillary suction time	CST
Chemical oxygen demand	COD
Diluted sludge volume index	DSVI
Nitrate	NO3
pH	pH
Polysaccharides	PS
Proteins	PR
Temperature	T
Time to filter	TTF
Total organic carbon	TOC
Total solids	TS
Transparent exopolymer particles	TEP
UV 240 nm	UV 240 nm
UV 254 nm	UV 254 nm
UV 280 nm	UV 280 nm
Volatile suspended solids	VSS

4.2.2.FOULING INDICATORS

4.2.2.1. DESCRIPTION OF THE STATISTICAL ANALYSIS

All results from the monitoring program were evaluated using the statistical tool SPSS 17.0. First, the matrix of correlation of the parameters was obtained. After that, a multiple linear regression was performed in which the independent variables (predictors) were parameters measured in the mixed liquor sludge supernatant and the dependent variable was the critical flux. The best fits indicated those variables which have more influence in the critical flux and thus in MBR sludge filterability and these were called fouling indicators.

4.2.2.1.1.UNIVARIATE ANALYSIS

The univariate analysis was performed by obtaining the Pearson matrix. For the evaluation of the correlation between the variables, the Pearson regression coefficient (r) is used, which is obtained by dividing the covariance of the two variables by the product of their standard deviations. The absolute value goes from 0 to 1, 1 being the best correlation possible. The sign of the coefficient indicates if the correlation is negative (when the independent variable increases the dependent decreases) or positive (the dependent variable increases when the independent increases). In this study, correlations with r coefficients of more than 0.8 were considered strong correlations, 0.6-0.7 were classified as medium and r coefficients of 0.5 or less indicated a weak correlation. Not only is the Pearson correlation important to evaluate the significance of the correlation but also the number of samples N. When both r and N are high, SPSS flag the correlation coefficient with one (medium significant correlation) or two (significant correlation) stars, as can be seen in some of the tables of this chapter. After obtaining the Pearson matrix, the best correlations with J_c indicated the highest influence in filterability of MBR sludge and were consequently selected as the best fouling indicators.

4.2.2.1.2.MULTIVARIATE ANALYSIS

As it was mentioned in the background chapter, fouling is a complicated issue and, when studying its origins, the interrelationship between the influencing parameters must be taken into account. This can be achieved using multivariate analysis. Multiple linear regression is a multivariate analysis which attempts to model the relationship between two or more explanatory variables and a response variable by fitting a linear equation. The model is evaluated using the R^2 coefficient, which indicates the proportion of variability in a data set that is accounted for by the statistical model. It ranges from 0 to 1, meaning a high R^2 coefficient (0.8-1) that the dependent variable can be satisfactorily predicted by the model. Classical assumptions for linear regression are:

- Linearity between the variables. It is assumed that the relationship between variables is linear. In practice this assumption can virtually never be confirmed, but multiple regression procedures are quite robust to minor deviations from this assumption. This can be examined by plotting the errors against the variables. These must not show any trend or pattern. To check this issue, The Durbin-Watson coefficient is used. This indicates the correlation between the residuals of the model. Values of 1-4 indicate possible relationships between residuals and a value lower than 1 indicates an important relationship between residuals.
- Normal distribution of the errors. This is checked by plotting the errors in a histogram and looking if they are normally distributed.

- The correlation between the predictors is not very high. If this is the case, the coefficients for the variables in the equation are not real as they depend on the other variables in the equation. As a consequence, the importance of the variable can be underestimated.

It was checked during this study that all these assumptions could be applied for the present data.

The standardized regression coefficients of the linear regression (beta coefficients) are calculated by subtracting the mean value and dividing by the standard deviation, so that they indicate the sensitivity of the dependent variable to each of the independent variables. Like the r coefficient, beta coefficients can go from -1 (negative correlation) to 1 (positive correlation). Higher values of beta indicate a greater impact on the dependant variable.

As each parameter was measured in a different day of the week, interpolation of data was performed in some cases in order to have data from all parameters measured in the same days. This was necessary for the multiple linear regression (rule of thumb: minimum 30 data).

Analysing the units separately using multivariate analysis was not applicable because the number of J_c values was less than 30 for every unit.

4.2.2.2. UNIVARIATE ANALYSIS

The univariate analysis was performed for all data obtained and for each plant separately. This way, the differences in results could be related to the specificities of the plants. Table 8 shows the best correlations found for all units against the filterability of the activated sludge expressed as J_c *in situ* and as J_c *ex situ*.

A detailed analysis of each relevant parameter from the univariate analysis is presented:

J_c ex situ:

The correlations for the J_c *ex situ* (using the *ex situ* test cell) were in all cases significantly worse than those obtained with the J_c *in situ (*measured with the BFM, *in situ* test cell*)*. This agrees with the low correlation coefficient between these two parameters (J_c *in situ* and J_c *ex situ*), which is only 0.45. The relationship between the J_c *in situ* and J_c *ex situ* in units MBR1 and MBR2 is higher than considering all units together, with a regression coefficient of 0.59. As it was already discussed in section 3.3.2.3, this may be attributed to the sludge storage time, which is much higher for the units MBR3 and MBR4. These units are located one hour away from the laboratory where the *ex situ* measurements are done, which may alter the properties of the activated sludge and therefore give altered filterability values.

Table 8. Best correlations against Jc in *situ* and *ex situ*.

		J_c *in situ*	J_c *ex situ*
J_c *ex situ*	r	0.452**	1.000**
	N	21	25
J_{ci-1} *in situ*	r	0.927**	0.269
	N	86	23
Temperature	r	0.566**	-0.207
	N	90	18
pH	r	0.259	0.414
	N	50	19
TEP coll.	r	-0.558**	0.129
	N	75	29
TEP rejection	r	-0.667**	-0.047
	N	75	0.724
PS 2 µm	r	-0.717**	-0.069*
	N	33	19
bTEP/TEP	r	0.773**	-0.139
	N	41	13

*Medium significance; **Significant; N=number of samples; r= Pearson coefficient

J_{ci-1}:

The parameter J_{ci-1} corresponds to the last J_c value measured before a generic value J_{ci}. The purpose of this introduced parameter was to take a look at the inertia of the data by plotting the data J_{ci} versus J_{ci-1}. If these two parameters presented a strong correlation that would mean that the parameter J_c does not experience rapid changes. In the present case, the critical flux showed a strong correlation with its last value measured (J_{ci-1}), even if this was taken with a difference of more than one week, which proved that the parameter is not excessively dynamic and can be therefore monitored on a weekly basis (as it was done in this study). When considering the units MBR1 and MBR2 together, the critical flux was more dynamic than when considering the four units together. This may be related to a lower SRT in these units, which means a more frequent biomass renewal, which may result in a higher variation of the sludge characteristics. This was supported by the results obtained from MBR3 and MBR4, which operated with much higher sludge age. For these two units, the big inertia of the J_c was remarkable, as it correlated strongly with the parameter J_{ci-1}.

Temperature:

The direct influence of the temperature on critical flux reported a correlation coefficient of 0.57. Although the critical flux values were temperature corrected, the factor temperature influenced almost all studied parameters in different ways, as it was

described in section 3.3.1.3. The MBR4 was the most affected by the temperature, with a Pearson correlation coefficient of 0.77.

pH:

The pH did not affect significantly the J_c values. However, the influence of this parameter on J_c is indirect, as it may affect other measured parameters like nitrate, polysaccharides, etc. When the correlation between pH and the rest of parameters was considered, the best correlation was found against PS filtrated through 10 µm and against rejection of proteins, the regression coefficient being around 0.6.

TEP:

The best parameter related to soluble TEP was the TEP rejection, showing a Pearson coefficient of -0.67. However, by plotting the TEP data versus J_c (Fig. 31) it can be clearly seen that the reason why the correlation between these parameters in not highly significant is that the relationship between them is not linear for J_c<10 L/(m^{2}h). Thus, when excluding those data when J_c<10 L/(m^{2}h), the obtained correlation coefficient is higher (Fig. 32) and it is even higher when only MBR3 and MBR4 are considered (Fig. 33). The reason why J_c data lower than 10 L/(m^{2}h) do not correlate with TEP may be attributed to the measurement protocol of the BFM, which started the critical flux tests at 5-10 L/(m^{2}h). The lowest limit of detection cannot therefore be applied when the activated sludge contains high levels of TEP (higher than 100 mg/L).

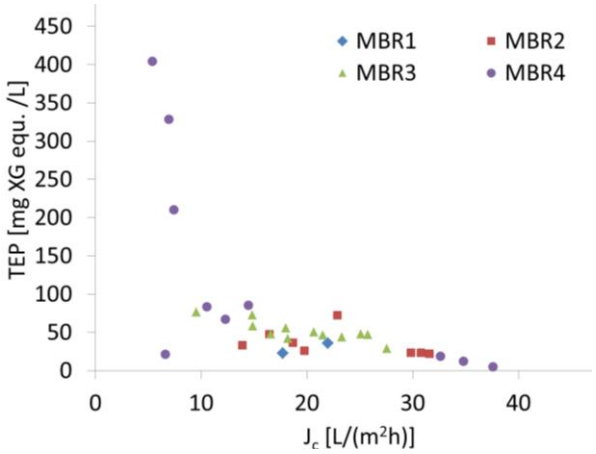

Fig. 31. TEP versus J_c, all MBR units.

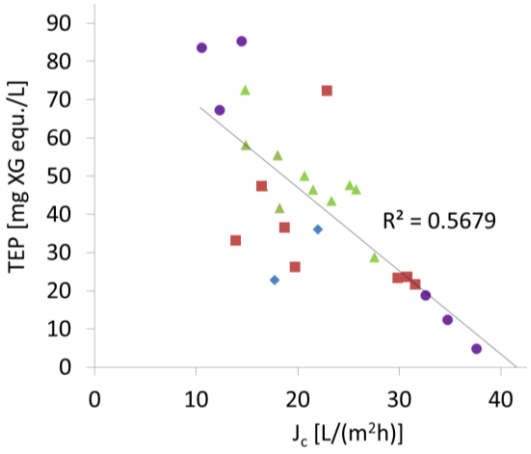

Fig. 32. TEP versus J_c. J_c values <10 L/(m^{2}h) not represented.

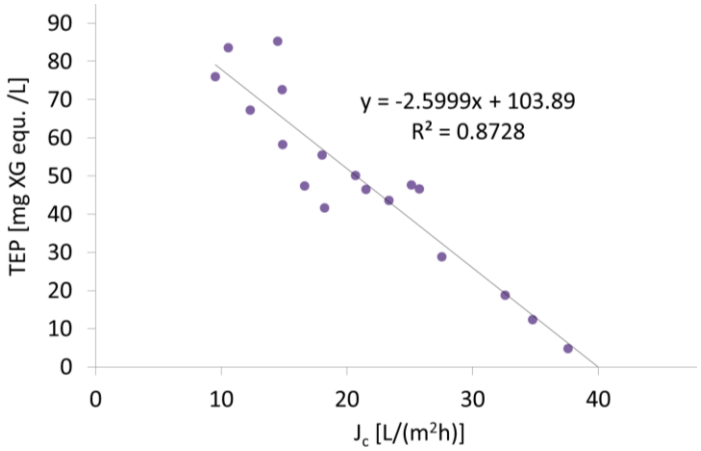

Fig. 33. TEP versus J_c for units MBR3 and MBR4. J_c values <10 L/(m^2h) are not represented.

The reason for a better correlation for the units MBR3 and MBR4 (R^2=0.87 versus R^2=0.60 for all units) is not clear. In chapter 3.3.1.1 it was mentioned that a higher SRT has been related to a lower correlation between fouling and SMP. This is in contradiction to the present results, which show a better correlation for TEP and filterability for MBR3 and MBR4, which operate at higher SRT than MBR1 and MBR2. An explanation for this may be that samples for TEP were not taken at the same moment as the J_c was measured, which may induce an error in the results. As MBR3 and MBR4 present a more stable sludge due to their higher SRT, they were less affected by this shift between J_c determination and sample grabbing.

When TEP was compared with PS, these two parameters seemed to correlate for the fraction of 10 µm but not for the rest of the fractions. There only exists a moderate correlation between TEP and PS, demonstrating that they are indeed different fractions of EPS. Slight relationships were found between proteins and TEP as well.

The differences between the fractions of TEP regarding to J_c were irrelevant, as they correlated to each other showing Pearson coefficients of 0.95 (TEP 0.2 µm - TEP 2 µm) and 0.88 (TEP 0.2 µm - TEP 10 µm). The same was observed for the other parameters and in general it can be said that no fraction was revealed as the key fraction for fouling. Slightly improved correlations were found when calculating the colloidal fraction of the polysaccharides, proteins and TEP compared to those correlations found with the PS, PR and TEP in the mixed liquor sludge supernatant.

It was interesting to observe that the bound compounds show a positive value of the correlation coefficient in all cases whereas soluble compounds present a negative value. This is in agreement with the literature, where higher concentrations of bound EPS can be found related to a more porous fouling layer and in consequence higher membrane filterability (Lee *et al.*, 2007).

bTEP/TEP:

The best fouling indicator was the ratio bTEP/TEP, with a correlation coefficient of 0.77 with the J_c *in situ*. When bTEP data were not interpolated, the number of data was lower but the correlation coefficient increased and it is presented in

Fig. 34. However, when considering the different MBR units separately, the ratio bTEP/TEP seemed only to influence MBR2 (r=0.63) and the difference is highly significant compared to MBR1 (r=0.18). The reason is unclear but it agrees with the fact that bTEP/TEP is related to flocculation and deflocculation processes, and these processes are different in these two plants, as MBR2 was treated during part of the monitoring campaign with different flux enhancers to improve filterability and flocculation.

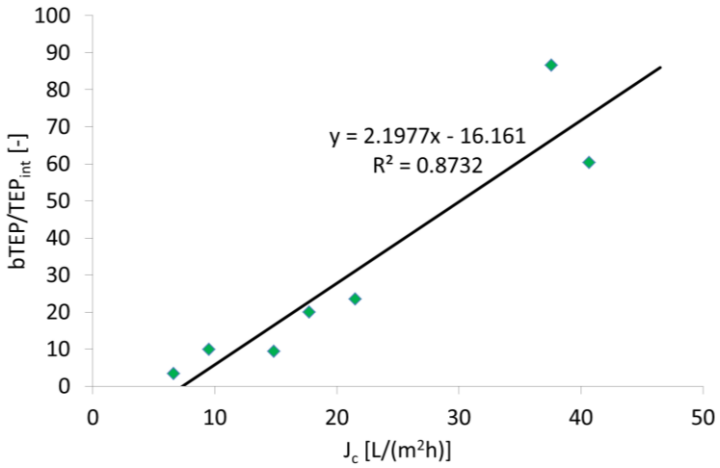

Fig. 34. bTEP/TEP versus Jc for all MBR units.

Polysaccharides:

After bTEP/TEP, the best fouling indicator was PS 2 µm, which presented a negative Pearson coefficient of -0.72. The correlation was stronger when taking only data from MBR2, where the correlation with PS 2 µm showed a Pearson coefficient of -0.84.

Proteins:

Proteins showed poor correlations against critical flux, with a maximum r of 0.45 found for the rejected proteins.

TS:

The total suspended solid were weakly correlated to the J_c of the plants. However, this parameter proved to be important in the multivariate analysis (section 4.2.2.3).

TTF, CST and DSVI:

Those parameters typically used for the quick evaluation of activated sludge filterability or settleability (TTF, CST, and DSVI) showed coefficients lower than 0.6 in all cases

and these were even lower when the parameters were normalised by dividing them by TS. An example of these weak correlations can be seen in Fig. 35 for the DSVI. An interesting correlation was found between TTF and colloidal PR, with a correlation coefficient of 0.84. Since in our study proteins did not seem to have any crucial influence on filterability (poor correlation between proteins and J_c) it is reasonable that, if proteins and TTF are strongly correlated, TTF do not show any important correlation with fouling either.

It was interesting to observe that TTF was highly related to critical flux for MBR3, with a correlation coefficient of 0.82, whereas it did not show any influence on J_c for the rest of MBR units. This may be attributed to a difference in the range of values of this parameter: while TTF values were for MBR1 and MBR2 plant normally between 20 and 50 s, in MBR3 it was constantly higher than 100 s due to its higher TS content. This seems to indicate that for high TS values cake fouling becomes the predominant fouling mechanism and, as TTF it is based on cake filtration, it can act as an easy indicator for MBR fouling at high TS values.

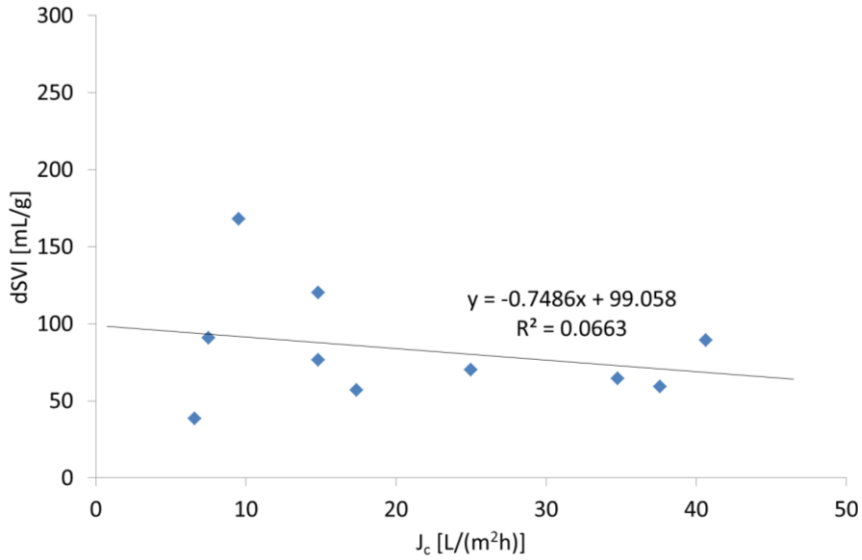

Fig. 35. Jc versus SVI for all MBR units (data not interpolated).

4.2.2.3. MULTIVARIATE ANALYSIS

As the highest correlation coefficient found applying univariate analysis was 0.8 it can be inferred that there is no unique variable which can explain the variations in J_c. Multivariate analysis of the data is then necessary in order to take into account the influence of many variables. As mentioned before, the multivariate analysis performed consisted in a multiple linear regression in which the dependent variable was the J_c and the beta coefficients indicate the sensitivity of the dependent variable to each of the independent variables, indicating higher absolute values of beta indicating a greater impact on the dependent variable.

The outcomes from the multiple linear regression resulted in a model with four predictors and a regression coefficient of 0.949 and is presented in Table 9.

Table 9. Outcomes of the multiple linear regression.

Parameter	Beta coefficient
NO_3	0.488
TEP	-0.596
T	0.566
bTEP	0.812

Four variables showed the highest influence on critical flux: TEP, bound TEP and temperature, nitrate. The regression coefficient represents the percentage of variance of J_c that can be explained by the predictors. In this case, the temperature and the concentration of bTEP, TEP and nitrate in the sludge supernatant could explain 95% of the variance in the J_c values. In Fig. 36, the J_c predicted obtained with the linear equation resulting from multivariate analysis using T, TEP, bTEP and NO_3 as predictors is presented.

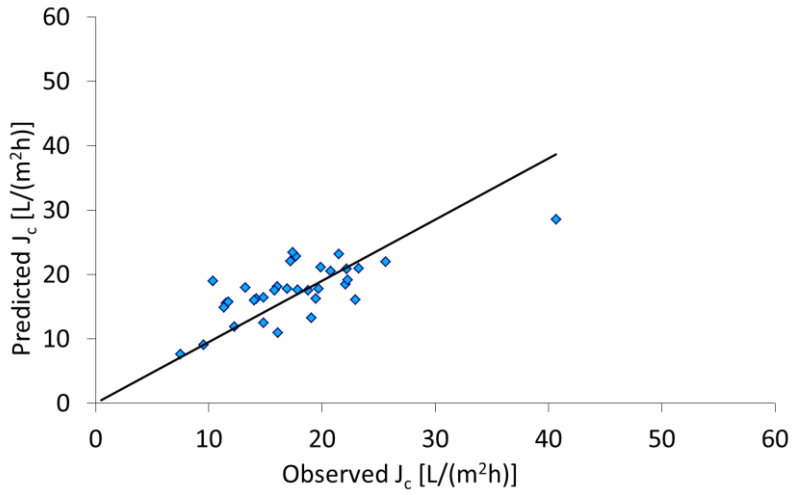

Fig. 36. Predicted versus observed Jc.

If we tried to introduce the parameter bTEP/TEP in the model, the correlation coefficients were lower than when using bTEP and TEP as individual parameters. This suggested that the reason why bTEP/TEP correlated so strongly in the univariate analysis is that using the combination of parameters bTEP and TEP, the influence of these two variables is taken into account and, as they are both important parameters for the filterability of the sludge, they result in better correlation coefficients together (expressed as a ratio) than alone. In the multivariate analysis they fit in the model better linearly (added up as separate variables) than as a unique variable (divided as a ratio).

The importance of the nitrate concentrations in the filterability of the sludge has been already discussed by Kim and Nakhla (2009), who found that the existence of a denitrification step has a negative effect on permeability. Drews *et al*. (2007) also observed that SMP increased when decreasing nitrates in a post-denitrification system. In this study, it has been demonstrated that the influence of nitrate on activated sludge filterability cannot be explained by its influence on SMP concentration, as this parameter shows a lower relationship with filterability than the concentration of nitrate.

TEP were more important for fouling than PS, proteins or total EPS; linear models that included TEP showed higher correlation coefficients than when including PS, proteins or total EPS. If TEP is replaced in the model for PS, the best fit was using the fraction PS 2 µm, showing an R^2 of 0.70.

The model improved (R^2=0.99) when, instead of TEP paper filtered, the variable TEP 2 µm was introduced, but the number of samples with data from these parameter was not enough to extract any representative conclusion.

4. SUMMARY AND CONCLUSIONS

The hypothesis of the existence of a unique parameter that can be used as an easy and quick fouling indicator in MBR could not be confirmed within this thesis. It was demonstrated that there is no single universal fouling indicator and the causes of fouling must be searched in the combination of several parameters. However, applying multivariate analyses the critical flux values could be correlated with four parameters measured in the activated sludge with a regression coefficient of 95%. Moreover, the statistical univariate analysis identified the ratio bTEP/TEP as the most significant factor for J_c, having a positive effect on sludge filterability. By analysing the meaning of these results, it can be found that bound compounds (here bTEP) are known to have a beneficial effect on filterability probably as a consequence of a more porous cake layer. On the other hand, higher concentrated soluble compounds (here lower bTEP/TEP ratio) are commonly related to lower filterability, which agrees also with the results obtained in this study. All this might indicate that they are only indirect fouling indicators, which actually only reflect the flocculation state of the activated sludge. In this study, TEP concentrations showed an important correlation with critical flux values, especially for the two MBR units treating domestic wastewater, for which the correlation coefficient was 0.87. Although PS concentration showed high correlations when plotted against J_c when performing multiple variable analyses, TEP which mainly covers the stickier polysaccharides fitted better in all cases. Thus, the novel parameter TEP showed up within this work as a novel key parameter for fouling investigations. This parameter not only appeared as more important than PS when analysing the results but it is also more practical to measure than the latter. TEP presents some advantages against the method for PS analysis: it is simpler and faster, the dye is non-toxic and no strong acids are used, so that there are no special residues after the test. Besides, no special correction is needed due to the presence of nitrate and nitrite in the sample.

Another parameter that significantly affected fouling was temperature. Even though J_c was temperature corrected, this parameter also influences several other factors like membrane resistance itself, nitrification, floc sizes and the release of EPS.

Although nitrate concentration showed a low correlation with J_c when considered as an individual parameter, it appeared to be relevant in the multivariate analysis. The mechanism by which this parameter influences filterability is not totally clear yet. It is known from the literature that SMP concentration is affected by nitrate but it is also known that nitrate affects filterability by other means and this was also supported by the results of the model obtained in this study.

The classical parameters for filterability and settleability taken from the CAS and commonly used for a quick evaluation of sludge filterability in MBR like TTF, CST and DSVI did not show any significant relationship with J_c of the sludge. Only TTF presented a high correlation with the critical flux for the MBR system that had a relatively high TS concentration (MBR3).

Comparing the influence of the individual parameters on J_c measured directly in the MBR (*in situ*) with test cell results (*ex situ*), a more significant correlation was always found for the *in situ* measurement. This indicates that *ex situ* test cell experiments are less representative for the fouling propensity of MBR activated sludge, which was attributed to the effect of the transportation and changes in the aeration on the biomass.

The BFM proved to be an interesting method for the evaluation of filterability of activated sludge as it was demonstrated with the validation against two other filterability characterization methods. As this tool measures the filterability on-line, it opens up the possibility of including the sludge filterability measured with the BFM in the control of an MBR system, permitting the adaptation of flux and/or aeration to the real-time sludge filterability. If the critical flux was low, using this control system the aeration could be accordingly increased or J could be decreased. On the contrary, if the filterability measured by the BFM was high, the aeration rate could be reduced or the flux increased. That would represent an optimization of the MBR operation and a reduction in operating costs, by reducing aeration costs. This would also avoid severe fouling, which could reduce chemicals costs and would consequently improve membrane longevity as the chemical cleaning frequency could be accordingly reduced.

5. MAIN SCIENTIFIC OUTCOMES OF THE STUDY

- The fouling parameters database acquired from the monitoring campaign represents the most extensive set of data to date in terms of number of parameters and MBR units studied. By evaluating these data, it was concluded that there is no unique parameter which can be used as universal fouling indicator, as many parameters have a great influence on fouling.
- A novel promising parameter, the TEP, has been introduced in MBR research and has been proved to be highly related to fouling in membrane bioreactors.
- Soluble and bound TEP, temperature and nitrate were revealed as most important parameters when considering fouling issues.
- The important relationship found between the ratio bTEP/TEP and fouling indicated that they are actually indirect indicators of the flocculation state of the activated sludge, meaning that this is a parameter which further investigations should point at.
- Classical filterability determination methods taken from the conventional activated sludge process like TTF, SVI and CST were only of limited use when evaluating fouling in the MBR units.
- It has been demonstrated that global parameters like proteins or polysaccharides indicate a sum of numerous compounds of different nature, which means a measurement of group of compounds of different fouling propensity. This may partly explain the controversy found in the literature about the correlation between EPS and fouling.
- A deeper study about the properties of the polysaccharides related to fouling revealed that the fouling propensity of the different polysaccharides depends on various parameters, the charge density and the gelling capacity being the most important ones.
- Three filterability characterization methods were compared with activated sludge from various MBR units. The results showed that the three methods are adequate for the evaluation of the fouling propensity of activated sludge in MBR.
- By comparing filterability data obtained with an *ex situ* and an *in situ* test cell, it was confirmed that *in situ* data are more reliable than *ex situ* when the storage time is long. This was attributed to the effect of the transportation and changes in the aeration on the biomass.
- A new tool for the evaluation of filterability of sludge in MBR, the BFM, was designed, developed and validated within this thesis. As this tool operates at similar conditions as an MBR unit, it can be used to obtain representative and comparable filterability data of membrane bioreactors. This is novel in the sector of MBR and represents an important step in the study of fouling and the monitoring of sludge filterability on-line.

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APPENDIX I: DESCRIPTION OF FILTERABILITY INDEXES

- **Capillary Suction Time (CST)**
  It is defined as the time to move activated sludge filtrate through capillarity between two electrodes. An activated sludge sample is poured in a test cell on a chromatography paper and the water from the activated sludge starts moving along the paper. The time it takes the water to move between two points marked on the paper is measured, which is called CST. It can be normalised by dividing by MLSS (g/L) in order to reduce the effect of MLSS. This parameter is generally used to estimate dewaterability of activated sludge. There exists a standard procedure (Clesceri *et al*., 1998) and a standard test device, which automatically gives the CST value in seconds.

- **Critical flux (J_c)**
  The critical flux is the flux at which fouling is first observed for a given feed concentration. A deeper discussion about this parameter can be found in chapter 3.3.2.4.

- **Modified Fouling Index (MFI)**
  The MFI is obtained after filtration using a 0.45 μm membrane filter and posterior plot of the ratio of filtration time and filtration volume as a function of total filtration volume. The slope of the linear region (cake filtration) of the curve obtained represents the MFI. It is generally normalised to 20ºC.

- **Sludge volume index (SVI) and diluted Sludge volume index (DSVI)**
  The sludge volume index (SVI) is the volume in mL occupied by 1 g of a suspension after 30 min settling divided by the suspended solids of the sample. If the SVI value is higher than 250 mL/L, the sample must be diluted with process effluent until the settled volume after 30 minutes is 250 mL/L or less and the parameter is then called DSVI. The SVI is typically used to evaluate roughly the settling characteristics of activated sludge and other biological solutions.

- **Specific Resistance (α)**
  The specific resistance can be obtained by plotting the ratio of filtration time and filtration volume as a function of total filtration volume. Using the following equation coming from Darcy's law, α can be calculated in the same way as MFI by obtaining the slope of the linear region of the curve of the graph t/V versus V.

$$\frac{t}{V_f} = \frac{\mu}{2}\frac{\alpha}{A^2 \Delta p} V_f(t) + \frac{\mu R_m}{A \Delta P} \qquad [6]$$

t= filtration time
V_f=volume of filtrate
μ=filtrate viscosity
A=area of the membrane filter
ΔP=differential pressure applied
α= specific resistance
R_m=membrane resistance

- **Time to Filter (TTF)**
  It is defined as the time needed to filter 100 mL of a 200 mL activated sludge sample using a gravity-driven funnel. It is the simplest index and its methodology is described in Standard Methods (Clesceri *et al*., 1998). In the standard method, a 90-mm Buchner funnel is used with Watman #1, #2 or equivalent filter papers and the pressure is fixed at 51 kPa or 7.4 psi. In this study, activated sludge was filtered at atmospheric pressure. The resulting TTF value can be normalised by dividing by the MLSS concentration of the sample in order to eliminate the effect of MLSS.

- **ΔR_{20}**
  This parameter expresses the increase in additional membrane filtration resistance after extracting of 20 L/m² of permeate. It represents the parameter obtained to characterize filterability of activated sludge using the DFCm, which is detailed in chapter 3.3.2.3 and 4.1.1. Normally a ΔR_{20} value below $0.2 \cdot 10^{12}$ m^{-1} is considered typical for good filterable mixed liquors, whereas ΔR_{20} values above $1 \cdot 10^{12}$ m^{-1} are characteristics of activated sludge with bad filterability.

- **VFM_{rev}**
  The VFM_{rev} is the reversible fouling propensity measured by MBR-VFM system, and it is expressed in %. It ranges from 0% (no fouling) to 100% (very high fouling). The measurement protocol consisted of the following 4 steps:

  - Conditioning: 5 min, air flow rate 500 ml min^{-1}.
  - Filtration: 15 min, TMP 0.10 bar, air flow rate 200 ml min^{-1}.
  - Relaxation: 10 min, air flow rate 500 ml min^{-1}.
  - Filtration: 5 min, TMP 0.10 bar, air flow rate 400 ml min^{-1}.

  The first filtration step is performed at low air flow rates in order to force reversible fouling. The second and third steps are conducted at high air flow rates to remove all reversible fouling. After data processing, the reversible fouling propensity is presented in a graph in which the normalized throughput of permeate is plotted versus the increased resistance due to reversible fouling. An image recognition program based on fuzzy set logic summarizes the complex fouling behavior represented by this graph into the normalized reversible fouling value (VFM_{rev}).

APPENDIX II: MONITORED PARAMETERS

Monitored parameters	Acronym	Sample
Biopolymers	Biopol	Filtered activated sludge (metallic filter 1 µm)
	$Biopol_p$	Permeate
Capillary suction time	CST	Activated sludge
Chemical oxygen demand	COD	Filtered activated sludge (paper filter)
	COD 10 µm	Filtered activated sludge (10 µm)
	COD 2 µm	Filtered activated sludge (2 µm)
	COD 0.2 µm	Filtered activated sludge (0.2 µm)
Diluted sludge volume index	DSVI	Activated sludge
Nitrate	NO3	Paper filtered activated sludge
pH	pH	Activated sludge
Polysaccharides	PS	Filtered activated sludge (paper filter)
	PS 10 µm	Filtered activated sludge (10 µm)
	PS 2 µm	Filtered activated sludge (2 µm)
	PS 0.2 µm	Filtered activated sludge (0.2 µm)
	PS_p	Permeate
	bound PS (or bPS)	Sludge pellet (centrifugated activated sludge)
Proteins	PR	Filtered activated sludge (paper filter)
	PR 10 µm	Filtered activated sludge (10 µm)
	PR 2 µm	Filtered activated sludge (2 µm)
	PR 0.2 µm	Filtered activated sludge (0.2 µm)
	PR_p	Permeate
	bound PR (or bPR)	Sludge pellet (centrifugated activated sludge)
Temperature	T	Activated sludge
Time to filter	TTF	Activated sludge
Total organic carbon	TOC	Filtered activated sludge (1 µm)
	TOCp	Permeate
Total solids	TS	Activated sludge
Transparent exopolymer particles	TEP	Filtered activated sludge (paper filter)
	TEP 10 µm	Filtered activated sludge (10 µm)
	TEP 2 µm	Filtered activated sludge (2 µm)
	TEP 0.2 µm	Filtered activated sludge (0.2 µm)
	TEP_p	Permeate
	bound TEP (or bTEP)	Sludge pellet (centrifugated activated sludge)
UV 240 nm	UV 240 nm	Filtered activated sludge (paper filter)
	UV 240 nm 10 µm	Filtered activated sludge (10 µm)
	UV 240 nm 2 µm	Filtered activated sludge (2 µm)
	UV 240 nm 0.2 µm	Filtered activated sludge (0.2 µm)
UV 280 nm	UV 280 nm	Filtered activated sludge (paper filter)
	UV 280 nm 10 µm	Filtered activated sludge (10 µm)
	UV 280 nm 2 µm	Filtered activated sludge (2 µm)
	UV 280 nm 0.2 µm	Filtered activated sludge (0.2 µm)
UV 254 nm	UV 254 nm 10 µm	Filtered activated sludge (10 µm)
Volatile suspended solids	VSS	Activated sludge

Calculated Parameters	Acronym	Calculation
Biopolymer rejection	$Biopol_{rej}$	$Biopol_{coll}$/Biopol
Bound to soluble TEP ratio	bTEP/TEP	bTEP/TEP
bound/soluble TEP ratio	bTEP/TEP	bTEP/TEP
Normalized CST	CST/TS	CST/TS
Normalized TTF	TTF/TS	TTF/TS
Polysaccharides colloidal	PS_{coll}	PS - PS_p
Polysaccharides rejection	PS_{rej}	PS_{coll}/PS
Protein rejection	PR_{rej}	PR_{coll}/PR
Proteins colloidal	PR_{coll}	PR - PR_p
TEP colloidal	TEP_{coll}	TEP - TEP_p
TEP rejection	TEP_{rej}	TEP_{coll}/TEP