DOTTORATO DI RICERCA IN INGEGNERIA CIVILE PER L'AMBIENTE ED IL TERRITORIO
XII Ciclo - Nuova Serie (2011-2013)
DIPARTIMENTO DI INGEGNERIA CIVILE, UNIVERSITÀ DEGLI STUDI DI SALERNO

INVESTIGATION OF INNOVATIVE SOLUTIONS FOR FOULING CONTROL IN MEMBRANE BIOREACTORS

STUDIO DI SOLUZIONI INNOVATIVE PER IL CONTROLLO DEL FOULING NEI BIOREATTORI A MEMBRANA

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In copertina: Membrane fouling development

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Finito di stampare il 31/01/2014

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ABSTRACT

Even though Membrane BioReactors (MBRs) are nowadays widely employed for municipal and industrial wastewater treatment, there is still a lack of understanding in several aspects. This is due to the complexity of the process, and its major drawback consists in a poor management of the fouling issue in many wastewater treatment plants. This is why researchers have put a great effort to understand MBR fouling in detail and to develop high-flux or low-cost membranes. In the last years, a number of studies have been published concerning fouling in MBRs, and this work aims to develop innovative ways to control fouling in Membrane BioReactors. It has to be noted that fouling phenomena are still hard to predict, given their dependence on a large number of elements.

Currently, full scale MBRs rely on physical and chemical cleaning protocols to reduce fouling that develops onto the membrane. Fouling causes TransMembrane Pressure (TMP) to rise up to levels that force plant managers to stop regular filtration and backwash/soak the unit using chemicals such as NaOCl, $C_6H_8O_7$ or $H_2C_2O_4$. Needless to say, this option raises operating costs and does not prevent fouling to develop further, once regular filtration is in place again. On the other hand, without such protocols membranes would fail soon because of sludging and subsequent drying phenomena that occur once solids accumulated at the bulk-membrane interface compress and prevent water to reach the membrane.

Many research studies aimed at enhancing cleaning protocols in MBRs, and many others focused on understanding this phenomenon. Despite all the effort put in this matter, the MBR industry still deals with the fouling issue in the same way. This work therefore aims to propose new ways to deal with the fouling issues, that might a) reduce the phenomenon in terms of its development on the membrane surface; b) reduce the compressibility of the fouling layer that develops onto the membrane; c) help tracking the development of the fouling layer and add information about the propensity of a sample to foul the membrane.

Research has been carried out at the University of Salerno, Italy (Sanitary Environmental Engineering Division – Civil Engineering Department) for the first two years, and at the University of Washington, US (Civil and Environmental Engineering Department) for the third year. Throughout the doctoral program, three different experimental setups have been developed:

- a first one composed of a membrane unit and a TMP transducer, to filter a solution that resembled a biological effluent from a urban wastewater treatment plant;
- a second one, a complete lab scale MBR that treats synthetic wastewater and can be remotely controlled through a sophisticated system of recording/storing data;
- a third one, still a complete lab scale reactor, henceforth named Bio-Entrapped Membrane Reactor (BEMR), in which a different biological degradation system has been introduced.

Results of the research activity pursued throughout the doctoral program can be summed up as follows:

- Results from the first phase show that significant reductions in TMP levels (up to 40% after 3 hours) can be achieved, the greatest enhancement being accomplished with larger nanoparticles, which provided wider channels for the bulk to filtrate.
- Results from the second phase show that the BEMR showed almost complete biodegradation of organic matter – feeding the reactor with a synthetic wastewater of 300 mg/L as COD. Residual COD in the biological effluent was due to detached biomass, as sCOD tests showed.
- TMP trends at 20, 30 and 40 LMH showed fair reduction of pressure values if compared to a conventional MBR. This result points out the benefits in terms of membrane life and operating costs of implementing BEMRs instead of conventional MBRs.
- Both MBR and BEMR produced primarily colloidal TEP, which likely caused membrane pores clogging.
- Results from the third phase, as the first attempt to monitor the TEP concentration in a BEMR, highlights the potential of this parameter as a fouling indicator for MBR/BEMR systems. TEP

showed the typical behavior of microbial by-products after experiencing a process disturbance, after which the concentration of TEP increased, whereas SMP concentrations in the units stayed stable.

- The BEMR produced less TEP than conventional MBRs due to slow-growing microorganisms with long SRT in the new bioreactor.

BEMR represents therefore an innovative way of dealing with the fouling issue. The implementation of entrapped biomass reduces the amount of biological degradation byproducts that eventually reach the membrane surface, therefore limiting fouling. Although the system has to be tested at full scale level, it looks promising for wastewater treatment and further research can develop further the idea.

SOMMARIO

Nonostante il diffuso impiego che i Membrane BioReactors (MBRs) trovano oggigiorno nel campo del trattamento delle acque reflue urbane e industriali, una fondamentale mancanza di comprensione di molteplici aspetti legati al processo compromette l'utilizzo di tali sistemi su larga scala, limitandone l'applicazione a realtà in cui sia possibile sostenere i più elevati costi di installazione e di gestione a fronte di una qualità maggiore dell'effluente finale. La principale criticità di tali sistemi è rappresentata senza dubbio dal fenomeno del fouling, o sporcamento, delle membrane destinate alla filtrazione del refluo. Una non corretta gestione dell'impianto, con conseguente insorgenza di fouling sino a livelli non tollerabili dal sistema, porta inevitabilmente alla perdita dell'integrita delle membrane e a gravi problemi di gestione legati alla qualità dell'effluente sversato nel corpo idrico.

E' da tale problematica, pertanto, che scaturisce l'intensa attività di ricerca che negli ultimi 15 anni ha caratterizzato il mondo scientifico nel campo del trattamento delle acque reflue urbane ed industriali. La possibilità di limitare o contrastare la formazione del fouling, nonché la volontà di comprendere appieno i meccanismi e le cause caratterizzanti detto fenomeno, rappresentano senza dubbio alcuno le *driving forces* che hanno supportato una vasta produzione a scala globale di articoli scientifici focalizzati su tale aspetto.

Ad oggi, resta sostanziale la difficoltà nel prevedere lo sviluppo del fenomeno del fouling nel tempo, ed i modelli disponibili in letteratura ancora non gestiscono appieno le molteplici variabili che caratterizzano il processo.

Il presente lavoro si configura pertanto come uno sforzo teso ad introdurre innovazioni nel campo del controllo del fouling in sistemi MBR.

Nonostante i numerosi studi compiuti in tale campo, i sistemi a scala reale continuano a prevedere protocolli di pulizia delle membrane essenzialmente basati su processi chimici e/o fisici, rimuovendo parte del fouling venutosi a creare. Ciò evidenzia la totale assenza di sistemi che vadano ad agire sulle caratteristiche del layer che viene a crearsi, e ancor più sul processo di formazione del fouling stesso, o in altri termini sulle

cause del fenomeno. La formazione del fouling in sistemi MBR comporta l'aumento dei livelli pressori (misurati come TransMembrane Pressure, o TMP), solitamente fino a valori tali da richiedere l'interruzione delle operazioni di filtrazione per lasciar spazio a procedure di lavaggio delle unità coinvolte; in aggiunta, l'aumento dei livelli pressori comporta anche un incremento dei costi energetici da parte delle opere elettromeccaniche a servizio del sistema MBR. Normalmente, il lavaggio chimico delle membrane prevede l'utilizzo di reagenti quali NaOCl, $C_6H_8O_7$ o $H_2C_2O_4$ per rimuovere la sostanza organica e/o inorganica depositatasi sulla membrana. Tali protocolli ovviamente portano ad un ulteriore aumento dei costi di gestione dell'impianto – che possono raggiungere valori insostenibili qualora si renda necessaria la sostituzione delle membrane per perdita dell'integrità fisica (solitamente causata da una non corretta gestione del fouling).

Il presente lavoro mira dunque al raggiungimento di tre macrobiettivi per individuare strategie innovative volte al controllo del fouling in sistemi MBR: a) ridurre la compressione del layer di fouling – dovuta alla filtrazione continua – che si crea sulla membrana; b) limitare lo sviluppo del fouling in termini di produzione dei metaboliti che originano la formazione del layer; c) individuare parametri indicatori in grado di consentire un monitoraggio efficace del flusso dei composti capaci di causare il fouling.

La ricerca portata avanti durante il Ph.D. program è stata sviluppata presso l'Università degli Studi di Salerno, Italia (Sanitary Environmental Engineering Division - Dipartimento di Ingegneria Civile) per i primi due anni del programma, e presso la University of Washington, Stati Uniti (Dipartimento di Ingegneria Civile e Ambientale) durante il terzo anno.

Durante il corso di dottorato, sono stati sviluppati tre diversi setup sperimentali :

- Un primo setup composto da un'unità a membrane e un trasduttore di pressione, al fine di trattare una soluzione sintetica rappresentante un effluente biologico;
- Un secondo setup, costituito da un MBR convenzionale a scala di laboratorio, al fine di trattare un refluo urbano sintetico, controllato da remoto attraverso un sistema di registrazione/memorizzazione di dati;

- Una terzo setup, costituito da un reattore a scala di laboratorio, d'ora in poi denominato Bio-Entrapped Membrane Reactor (BEMR), nel quale è stato introdotto un innovativo sistema di degradazione biologica.

I risultati dell'attività di ricerca svolta nel corso del programma di dottorato possono essere riassunti come segue:

- I risultati della prima fase indicano che riduzioni significative dei livelli pressori come TMP (fino al 40 % dopo 3 ore) possono essere raggiunti mediante l'impiego di nanomateriali atti a prevenire la compressione del fouling.
- I risultati della seconda fase mostrano che il sistema BEMR porta ad una quasi totale degradazione biologica della sostanza organica – il reattore è alimentato con un refluo sintetico pari a 300 mg/L come COD.
- I trend di TMP a 20, 30 e 40 LMH ottenuti utilizzando un sistema BEMR mostrano una congrua riduzione dei valori di pressione rispetto ad un MBR convenzionale. Tale risultato evidenzia i vantaggi in termini di vita delle membrane e di riduzione dei costi operativi grazie all'impiego di sistemi BEMR.
- Sia l'MBR convenzionale che il BEMR producono TEP di natura principalmente colloidale, che probabilmente rappresenta la principale causa di fouling sulle membrane.
- Il monitoraggio della concentrazione di TEP in un BEMR (terza fase) mette in evidenza le potenzialità di questo parametro come indicatore del fouling per i sistemi MBR/BEMR. I TEP mostrano il comportamento tipico dei sottoprodotti dell'attività batterica dopo aver sperimentato un disturbo, dopo il quale si assiste ad un nuovo aumento delle concentrazioni di TEP, mentre le concentrazioni di SMP nel sistema sono rimaste costanti.

Il sistema BEMR rappresenta quindi una soluzione innovativa per fronteggiare il problema del fouling. Lo sviluppo di biomassa in forma confinata riduce la quantità di sottoprodotti della degradazione biologica che raggiungono la superficie della membrana, limitando quindi il fouling. Il sistema dovrà comunque essere testato a scala reale, per cui ulteriori ricerche ed approfondimenti si rendono necessari per valutare le potenzialità effettive del sistema, anche in termini economici.

ACKNOWLEDGMENTS

This dissertation is among the most significant achievements I have ever accomplished. Although only my name appears on the title page of this dissertation, a great many people have contributed to this work and to my wonderful graduate experience, to whom I would like to express my sincere appreciation and gratitude.

My deepest gratitude goes to my advisor, Prof. Vincenzo Belgiorno, for his guidance, encouragement, and endless trust during my Ph.D. program at University of Salerno. I feel incredibly privileged to have had him as my advisor. I am also grateful to the faculty members at both the University of Salerno and University of Washington. Particularly, I would like to acknowledge Dr. Vincenzo Naddeo as my co-advisor for the many valuable discussions that helped me understanding my research better and introduced me to the research world. I have been fortunate enough to work under Dr. Mark Benjamin's supervision, and he deserves my deepest appreciation.

I also want to thank my fellow Ph.D. students and the whole research team at SEED that supported me over these three years. Particularly, I want to thank Stefano for having been a great colleague, and even more an amazing friend. At the same time, my gratitude goes to all my friends, who cheered me up many times and helped me over the years.

My fiancee, Giulia, has been a source of support and encouragement throughout the years that I devoted to my Ph.D. program. Her tolerance of my long hours spent in the lab and bad moods is a testament of her love and devotion, which I will cherish forever. I gratefully and sincerely thank my dear parents, for having nurtured me. Finally, I thank my little brother, Lorenzo, for always being my inspiration to succeed.

ABOUT THE AUTHOR

Davide Scannapieco received his B.Sc. at University of Salerno in 2008. In 2010 completed his M.Sc. in Environmental Engineering at University of Salerno, after carrying out research about Advanced Oxidation Processes at Cranfield University (UK), where he wrote his thesis. In 2011 was admitted to the Ph.D. program at University of Salerno, and since then he has been working mainly on Membrane BioReactors (MBRs) and the related fouling issue.

Throughout the doctoral program, he has been researching on several subjects, such as Water Framework Directive implementation, water quality assessment, Life Cycle Assessment, Environmental Impact Assessment and waste management. He has been co-advisor for 5 B.Sc. and 1 M.Sc. theses, teaching assistant for a B.Sc. class, speaker at 5 international conferences and author or coauthor of 13 scientific papers published on ISI journals.

Davide Scannapieco si è laureato con lode nel 2010 in ingegneria per l'ambiente e il territorio, discutendo una tesi dal titolo "Trattamento di acque contaminate da pesticidi: processi di fotocatalisi UV/TiO_2" completata presso la Cranfield University (UK). Nel 2011 è stato ammesso a frequentare la Scuola Dottorale in Ingegneria presso l'Università degli Studi di Salerno. Il suo principale campo di ricerca è l'analisi del fouling in sistemi MBR.

Durante il programma di dottorato, molteplici sono state le tematiche appartenenti dall'Ingegneria Sanitaria Ambientale che sono state affrontate: implementazione della Water Framework Directive, valutazione della qualità dei corsi d'acqua, Life Cycle Assessment, Valutazione di Impatto Ambientale e gestione dei rifiuti solidi. E' stato correlatore per 5 tesi di primo livello e 1 tesi di secondo livello, assistente d'aula per un corso, speaker presso 5 convegli internazionali e autore o coautore di 13 pubblicazioni scientifiche su riviste ISI.

1 INTRODUCTION

Membrane BioReactors (MBRs) and their main advantages have been discussed in the scientific literature in the last years. Basically, MBRs are an hybrid process that consists of a Conventional Activated Sludge (CAS) stage coupled with physical separation through a membrane filtration step that aims to retain the biomass and concentrate it up, therefore reducing the oxidation tank size and enhancing the efficiency of the biological process (Judd, 2010; Santos et al., 2011; Monclus et al., 2011; Brepols et al., 2008; Drews, 2010). The introduction of MBRs into wastewater treatment plants leads to the elimination of secondary clarifiers and tertiary filtration processes (Figure 1-1), reducing plant footprint and limiting capital expenditure (Ng and Kim, 2008).

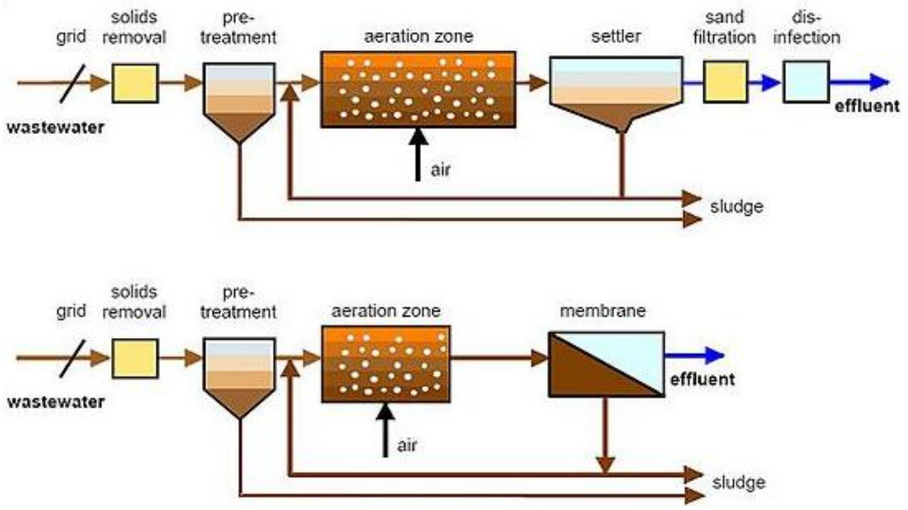

Figure 1-1 - Comparing flowcharts of a CAS (upper) treatment with an MBR (lower)

Moreover, given the provided permeate quality of MBRs, their effluent is typically suitable for reuse applications, (Arevalo et al., 2009; Zanetti et al., 2010), providing a barrier to certain chlorine resistant pathogens such

as Cryptosporidium and Giardia (Ottoson et al., 2006; Williams and Pirbazari, 2007; Marti et al., 2011; Simmons et al., 2011).
Consequently, the MBR market has registered, over the last years, an average growth rate of roughly 11% per annum, and this is by far the best performance in terms of acquired market shares amongst wastewater treatment processes and membrane technologies (Judd, 2006; Judd, 2008). Table 1-1 shows a number of large full scale MBR plants recently commissioned worldwide, especially in water-stressed, oil-producing countries such as UAE and Qatar.

Table 1-1 - Recently commissioned MBR plants worldwide (adapted from Scannapieco et al., 2012)

Plant name	Location	Built in	Max flow rate [m^3/d]
Jumeirah Golf Estates	UAE	2010	220000
Palm Jebel Ali	UAE	2010	220000
Brightwater	US	2010	144000
Jebel Ali Free Zone	UAE	2007	140000
International City	UAE	2007	110000
Johns Creek	US	2007	93500
Beixiaohe	China	2007	80000
Al-Ansab	Oman	2006	78000
Peoria	US	2007	75700
Lusail	Qatar	2007	60200
Quinghe	China	2007	60000

The market is currently assumed to double every seven years. Based on installed membrane surface, the municipal sector holds 75% of the total MBR market volume (Yang et al., 2006; Lesjean and Huisjes, 2008).

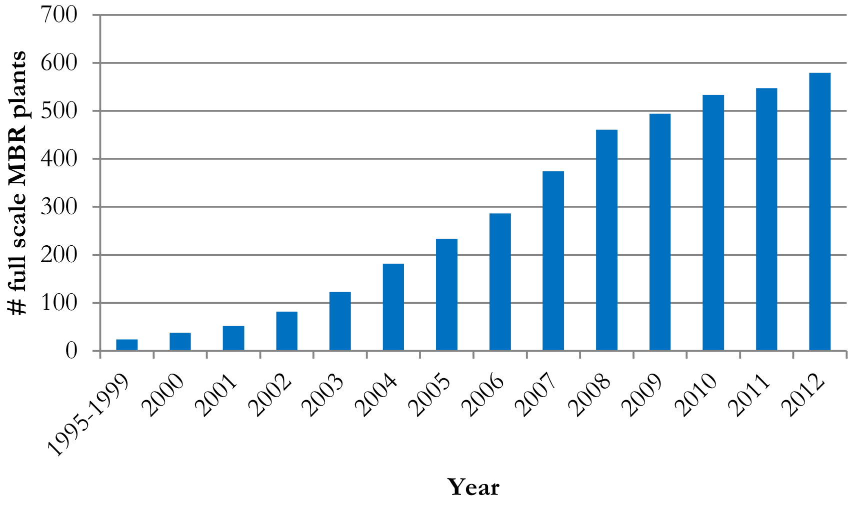

Figure 1-2 – Cumulative number of full-scale MBR plants

Figure 1-2 shows the cumulative number of MBR plants in the last decade. The semi-plateau reached in the last 2-3 years could be attributed to the 2008 economic crisis that diverted public spending and prevented investment in the water sector.

Figure 1-3 - Membrane BioReactor installation (courtesy of GE Water, US)

The main drawback of MBR technology in comparison to CAS processes still is its high cost in terms of operational expenditure, mainly because of additional costs related to scouring and cleaning protocols (Judd, 2010; Drews, 2010). While membrane module costs have dramatically decreased over the last years leading to lower capital costs, membrane fouling abatement procedures generated elevated energy demands and became the main contribution to overall MBR operating costs. In addition, during MBR operation membrane fouling arises, reducing the permeate flux in value, or increasing the TransMembrane Pressure (TMP) and the energy required. This event may ultimately lead to membrane failure (Figure 1-4), but even in its early stage, it can determine serious problems for the MBR unit, also in terms of energy expenditure.

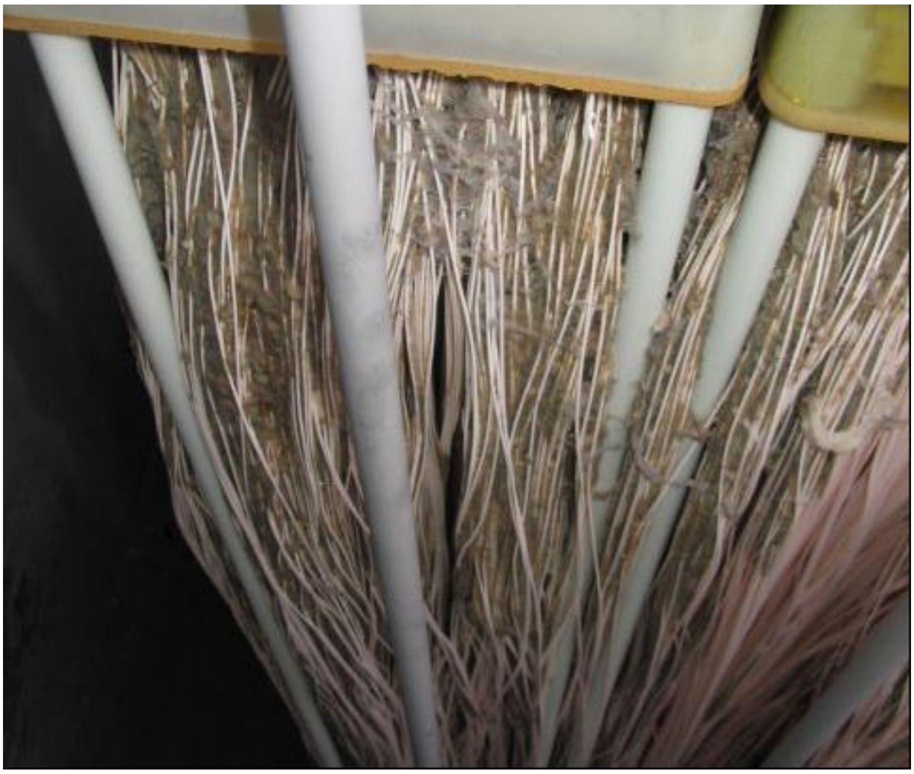

Figure 1-4 - Typical membrane failure due to fouling development and subsequent dewatering (courtesy of Huber Technology, Germany)

As for the design, the MBR management has been optimized over the last years, thanks to the significant experience gained in the field of MBR processes. Nevertheless, the management of these systems is still driven by empirical considerations because of their complexity, since both biological oxidation and membrane filtration occur at the same time. What is more, when compared to CAS systems, it is generally recognized that MBRs generate higher operative expenditure, mostly because of membrane aeration (Judd, 2010; Germain et al., 2005; Brepols et al., 2008). Even though the biological and membrane stages occur in the same space, they cannot be regarded as separate unit operations, since they continuously interact with each other. Notwithstanding their known advantages (e.g. reduced excess sludge production), arbitrarily high mixed liquor suspended solids (MLSS) concentrations are not typically employed because of resulting lower aeration rates and increased non-

Newtonian viscosities at higher MLSS concentrations (Rosenberger and Kraume, 2002). A high value of viscosity affects the energy required for pumping, as well as the air scouring effect and oxygen supply for the microorganisms. As a consequence, nowadays full scale MBRs treating municipal wastewater are operated in an MLSS range of roughly 8000–14000 mg/L (Judd, 2010; Brepols et al., 2008; Kraume et al., 2009; Bracklow et al., 2008). Figure 1-5 shows CAS and MBR liquors and their difference in color, and therefore in MLSS, which means that MBR (dark brown) liquor has also higher viscosity.

Figure 1-5 - Differences in color and viscosity in CAS (left) and MBR (right) oxidized liquor

This is a wide range, in that the optimum value depends on the specific installation features, such as pumps, aeration systems and other biomass characteristics.

Concerning MBRs, models and parameters describing either biological reactions or membrane filtration have been used extensively in several works (Hlavacek and Bouchet, 1993; Chudacek and Fane, 1984; Elmaleh and Ghaffor, 1996). However, since the biological and membrane filtration stages affect each other, a revision of such models in order to allow their application to MBR systems is needed (Drews and Kraume, 2005; Saroj et al., 2008). Although several practical experiences and data are available for MBR processes, very little investigation taking into account all interactions has been carried out so far.

1.1 OBJECTIVE

This work aims to critically review research findings in the MBR field. In particular, the main goal of this work is to discuss the membrane fouling phenomenon, and its control in MBRs. In addition, the state of the art of MBR systems, the fouling control procedures in MBRs, and the importance of fouling agents has been discussed.

The research activity pursued throughout the Ph.D. program and hereafter described aimed to find alternative ways to reduce, control and contrast fouling in MBRs, with a main focus on biological oxidation and fouling indicators. A comparison between conventional MBRs and Bio-Entrapped Membrane Reactors (BEMRs), in which the activated biomass is confined into carriers, has been discussed in terms of differences in fouling development on the same membrane.
To this extent, three different experimental setups have been developed, in order to deepen the knowledge of the following issues:

- Whether it is possible to apply a coating onto the membrane using inert nanoparticles, as to prevent the fouling layer compression due to filtration;
- Whether it is possible to introduce a different biological oxidation step, and subsequently modify the fouling rate in the membrane unit;
- Whether it is possible to monitor the fouling development through an innovative parameter (Transparent Exopolymer Particles, TEP), as to prevent severe fouling and increase physical/chemical cleaning frequency.

The present document has therefore been divided in six chapters. In Chapter 2, background information is provided about membrane filtration, MBRs, their pros and cons, fouling in MBRs and ways to cope with it. In Chapter 3, Materials and Methods of the experiments have been described for each of the three phases of the research activity, carried out both in Salerno, at the Sanitary Environmental Engineering Division (SEED) and in Seattle, at the Civil and Environmental Engineering Department of the University of Washington. In Chapter 4 results are presented and discussed for each of the three phases in which the research has been divided. Finally, In Chapter 5 conclusions are drawn and suggestions for further research are pointed out.

2 BACKGROUND INFORMATION

2.1 MEMBRANE BIOREACTORS (MBRS)

MBRs represent an acknowledged key treatment process for wastewater reclamation and water recycling, as they offer the advantages of biomass separation and concentration (Hai et al., 2011). MBRs represent an absolute barrier to solids and microorganisms thus providing a removal system of high mixed liquor suspended solid concentration, which can even reach 30 g/L in industrial applications (Judd, 2010).

The initial concentration and removal efficiency of pollutants by Membrane BioReactors are not directly associated, but chemical and physical properties of pollutants that are present in wastewater have been linked to MBR removal efficiencies. The primary removal of particles in MBR systems is achieved by sieving through hydraulic force on the wastewater over the membrane. All large molecules are collected at the membrane/bulk separation surface, as they cannot pass through. Hence the separation of suspended solids is not limited merely to the sludge settling properties but to filtration characteristics of the MBR, which will define the separation efficiency. The membrane has to be strong enough to hold the hydraulic pressure exerted by the wastewater shear force and the pore size and membrane material will determine filtration efficiency (Judd, 2010). Generally, the pore size used is under 0.1 μm, so that the MBR produces a clarified and disinfected effluent. It also concentrates the biomass, which results in a reduced necessary tank size and increase in the efficiency of the bio-treatment process. The treated water is of high purity in respect to dissolved constituents such as organic matter and ammonia, which are significantly removed (Chang et al., 2002; Drews et al., 2009). To assess the effectiveness of MBR removal efficiency, the effluent can be analyzed to examine its physical qualities. As a result, BOD, COD, NH_4, TOC and TSS measurements result in high quality of the effluent for many full-scale applications (Radjenovic et al., 2009).

2.1.1 Fundamentals

The key elements of any membrane process relate to the influence of the following parameters on the overall permeate flux (Judd, 2010):

(a) the membrane resistance,
(b) the operational driving force per unit membrane area,
(c) the hydrodynamic conditions at the membrane:liquid interface,
(d) the fouling and subsequent cleaning of the membrane surface.

The flux (normally denoted J) is the quantity of material passing through a unit area of membrane per unit time. This means that it takes SI units of $m^3/m^2/s$, or simply m/s and is occasionally referred to as the permeate – or filtration – velocity. Other non-SI units used are litres per m^2 per hour (or LMH) and m/day, which tend to give more accessible numbers: MBRs generally operate at fluxes between 10 and 100 LMH (Judd, 2010; Drews, 2010). The flux relates directly to the driving force (i.e. the TMP for conventional MBRs) and the total hydraulic resistance offered by the membrane and the interfacial region adjacent to it.
Although for conventional biomass separation MBRs the driving force for the process is the TMP, for extractive or diffusive MBRs it is respectively the concentration or partial pressure gradient. Whereas with conventional pressure-driven MBRs the permeate is the purified product, for extractive MBRs the contaminants are removed from the water across the membrane under the influence of a concentration gradient and are subsequently biologically treated, the retentate forming the purified product. For diffusive bioreactors neither water nor contaminants permeate the membrane: in this case the membrane is used to transport a gas into the bioreactor.
Resistance R (/m) and permeability K (m/(s bar), or LMH/bar in non-SI units) are inversely related. The resistance is given by:

$$R = \frac{\Delta P}{\eta J}$$

where η is the viscosity (kg/(m s^2)) and ΔP (Pa) the pressure drop, and can refer to either the TMP (ΔP m Pa/bar in non-SI units) or individual

components which contribute to the pressure drop. Permeability is normally quoted as the ratio of flux to TMP (hence J/ΔPm), the most convenient units being LMH/bar, and sometimes corrected for temperature impacts on viscosity.
The resistance R includes a number of components, namely (Scannapieco et al., 2013):

(a) The membrane resistance,
(b) The resistance of the fouling layer (adsorbed onto the membrane surface),
(c) The resistance offered by the membrane:solution interracial region.

The membrane resistance is governed by the membrane material itself: mainly pore size, surface porosity (percentage of the surface area covered by the pores) and membrane thickness play a role in resistance. The fouling layer resistance is associated with the filtration mechanism, which is then dependent on the membrane and filtered solids characteristics. The membrane:solution interfacial region resistance is associated with concentration polarization (CP) which, for the more perm-selective processes such as RO, produces a solution osmotic pressure at the membrane surface which is higher than that in the bulk solution. The resistance offered by foulants is often further delineated into generic types according to their characteristics, behavior and origin. However, in general, the membrane resistance only dominates when fouling is either absent (i.e. the feedwater is almost free of fouling materials) or is suppressed by operating under specific conditions (Kim et al., 2008). Conventional pressure-driven membrane processes with liquid permeation can operate in one of two modes. If there is no retentate stream then operation is termed "dead-end" or "full-flow"; if retentate continuously flows from the module outlet then the operation is termed crossflow, as shown in Figure 2-1.

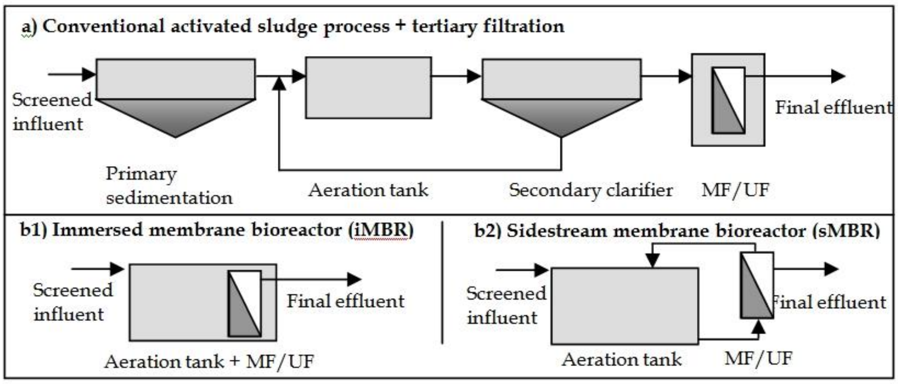

Figure 2-1 - CAS process (a) versus immersed (b1) and sidestream (b2) MBR (from Opentech)

Crossflow implies that, for a single passage of feedwater across the membrane, only a fraction is converted to permeate product. This parameter is termed the "conversion" or "recovery". The recovery is reduced further if product permeate is used for maintaining process operation, usually for membrane cleaning (Judd, 2010).

Filtration always leads to an increase in the resistance to flow. In the case of a dead-end filtration process, the resistance increases according to the thickness of the cake formed on the membrane, which would be expected to be almost proportional to the total volume of filtrate passed. Rapid permeability decay then results, at a rate proportional to the solids concentration and flux, demanding periodic cleaning (Figure 2-2).

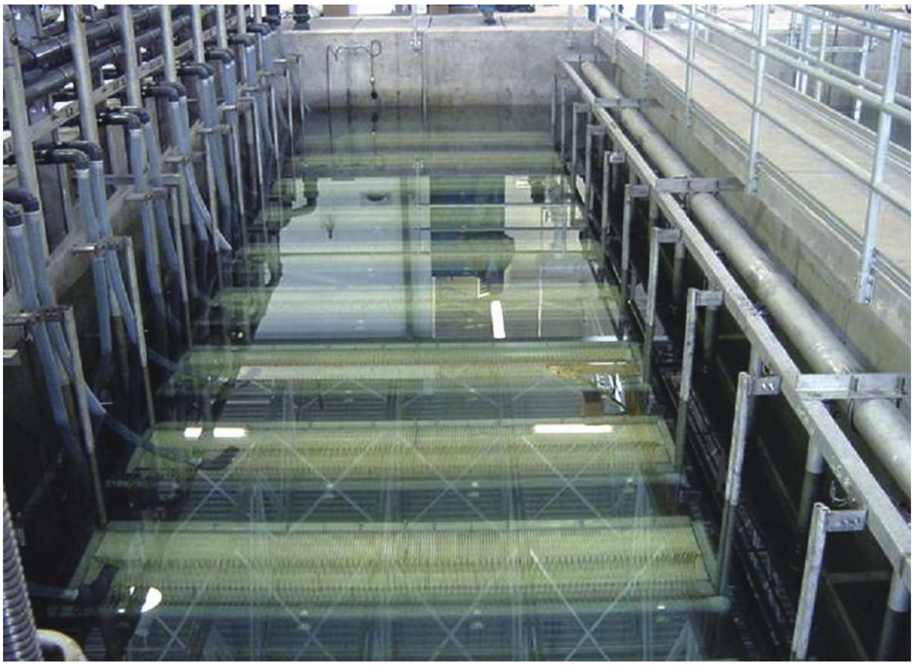

Figure 2-2 - MBR chemical cleaning, in which the modules are soaked into a sodium hypochlorite solution (courtesy of Ovivo, Australia)

For crossflow processes, this deposition continues until the adhesive forces binding the cake to the membrane are balanced by the scouring forces of the fluid (either liquid or a combination of air and liquid) passing over the membrane. All other things being equal, a crossflow filtration process would be expected to attain steady-state conditions determined by the degree of CP. In practice, only pseudo-steady-state (or stabilized) conditions are attained to do the unavoidable deposition or adsorption of fouling material. Filtration proceeds according to a number of widely recognized mechanisms, which have their origins in early filtration studies (Grace, 1956), comprising (Figure 2-3).

- complete blocking
- standard blocking
- intermediate blocking
- cake filtration

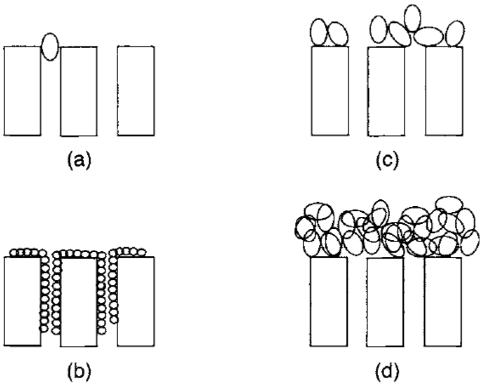

Figure 2-3 - Fouling mechanisms: (a) complete blocking, (b) standard blocking, (c) Intermediate blocking, (d) cake filtration (adapted from Judd, 2010)

All models imply a dependence of flux decline on the ratio of the particle size to the pore diameter. The standard blocking and cake filtration models appear most suited to predicting initial flux decline during colloid filtration (Stephenson et al., 2000; Xing et al., 2000) or protein filtration (Bowen et al., 1995). All of the models rely on empirically derived information and some have been refined to incorporate other key determinants.

On the other hand, a number of empirical and largely heuristic expressions have been proposed for particular matrices or applications. Classical dead-end filtration models can be adapted for crossflow operation if the proportion of non-deposited solute material can be calculated.

Monod kinetics can be used to design biological systems for a limiting substrate (S kg/m^3), usually organic carbon provided as BOD or COD. Using known biokinetic constants, the system kinetics and system mass balance can be used to define the rate of substrate degradation, biomass growth and sludge production (Reinthaler et al., 2003).

A full description of Monod kinetics for process design can be found in Metcalf and Eddy (2003).

The rate biokinetics determine the loading rate (the rate at which organic matter is introduced into the reactor, kg BOD/m^3), as determined by

Monod kinetics. Accordingly, the rate of reaction is first order with respect to a limiting substrate up to a maximum specific growth rate, after which growth is unaffected by any increase in substrate concentration:

$$\mu = \frac{\mu_M S}{K_S + S}$$

Where μ is the growth rate (/h), and μ_M is the maximum specific growth rate (/h), S is the limiting substrate concentration (g/m^3) and K_S is the saturation coefficient (g/m^3). It follows that there is a maximum specific substrate utilization rate, which is defined as:

$$k = \frac{\mu_M}{Y}$$

Where Y is the biomass yield (i.e. the mass of cells formed per mass of substrate consumed) (g Volatile suspended solids (VSS)/g BOD). Y can be controlled by manipulating environmental factors such as temperature and pH, but such changes are detrimental to biodegradation in the reactor (Eckenfelder and Grau, 1998). Substituting terms defined by Monod kinetics into a mass balance expression for the system and rearranging produces an expression in terms of effluent dissolved substrate S_e in g/m^3:

$$S = \frac{K_S(1 - k_e\theta_x)}{\theta_x(Yk - k_e) - 1}$$

where θ_x is the SRT or sludge age (/day) and k_e is the death rate constant. SRT is an important design parameter used for suspended growth systems. One of the advantages of an MBR system is that all of the solids are retained by the membrane, which affords the operator complete control over the SRT. The death rate constant accounts for endogenous metabolism, i.e. the utilization by cells of stored materials. The presence of extracellular polymerics associated with the biomass, k_e also accounts for grazing of the biomass by predatory organisms. For conventional activated sludge and anaerobic processes, k_e is typically in the range 0.04-0.075/day (Guo, 2006; Metcalf and Eddy, 2003), and takes similar values for MBRs (Fan et al., 1996; Wei et al., 2003). Experiments by Huang et al. (2001) showed that the endogenous decay in an MBR is higher (0.05-0.32/day) than for an ASXP (0.04-0.075/day).

Y_{obs}, the observed yield (g/(g/day)), is always lower than Y due to the effects of cell decay (k_e). The relationship between Y_{obs} and Y is governed by the SRT, θ_x, and is defined by:

$$Y_{obs} = \frac{Y}{1 + k_e\theta_x} + \frac{f_d k_e Y \theta_x}{1 + k_e\theta_x}$$

where f_d is the fraction of the biomass that remains as cell debris, usually 0.1-0.15 g VSS/g substrate (Metcalf and Eddy, 2003). Observed yields (Y_{obs}) are approximately 0.6/day for conventional aerobic processes and an order of magnitude lower for anaerobic ones. Y_{obs} is used to calculate the amount of heterotrophic sludge that will be produced by a biological system ($P_{x,het}$) for a given flow rate (m^3/day):

$$P_{x,het} = Y_{obs}Q(S - S_e)$$

The observed yield is the increase in biomass from heterotrophic cells only. Nitrification sludge and non-biodegradable solids also influence the total daily sludge production. P_x is the total sludge yield from substrate degradation and originates from the heterotrophic sludge yield ($P_{x,het}$) and the nitrification sludge yield ($P_{x,aut}$). The sum of all solids generated each day the non-biodegradable solids is:

$$X_0 = (TSS - VSS)Q$$

The sludge production from biodegradation in an MBR can be reduced to zero by controlling SRT (θ_x), k_e and Y. The change in θ_x has by far the greatest impact on sludge production (Xing et al., 2003) and mixed liquor suspended solids (MLSS).

Experience allows designers to set a desired MLSS concentration (X g/m^3). The MLSS then affects sludge production, aeration demand and membrane fouling and clogging. Using a design MLSS and SRT the aeration tank volume can be calculated by obtaining the mass of solids being aerated, and then using the MLSS to convert that mass to the volume, which those solids occupy:

$$V = \frac{(P_x + X_0)\theta_x}{X}$$

SRT and F:M ratio

The slow rate of microbial growth demands relatively long HRTs (compared with chemical processes), and hence large-volume reactors. Alternatively, retaining the biomass in the tank either by allowing them to settle out and then recycling them, as in an CAS process, fixing them to porous media, or selectively rejecting them, as with an MBR, permits longer SRTs without requiring the HRT to be commensurately increased. Controlling the SRT in a biological system allows the operator to control the rate of substrate degradation, biomass concentration and excess sludge production. The SRT is controlled by periodically discharging some of the solids from the process:

$$\theta_x = \frac{VX}{Q_W X_W + Q_E X_E}$$

where V and X are the aeration tank volume (m^3) and MLSS (g/m^3), Q_W and X_W the sludge wastage rate (m^3/day) and suspended solids concentration (g/m^3), and Q_E and X_E the corresponding values for the effluent. SRT should thus in theory determine the final effluent quality, though in practice effluent quality is determined by sludge settlability. In an MBR system, no solids can pass through the membrane (i.e. X_E=0), and hence the SRT is defined only by the wasted solids. If the solids wasted from the reactor are at the same concentration as those in the reactor, that is, $X_W = X$, the volume of sludge wasted Q_W becomes:

$$Q_W = \frac{V}{\theta_x}$$

An often-quoted CAS empirical design parameter is the food-to-microorganism ratio (F:M in units of inverse time), which defines the rate at which substrate is fed into the tank (SQ, Q being the volumetric feed flow rate in m^3/day) compared to the mass of reactor solids:

$$F{:}M = \frac{SQ}{VX}$$

This relates to SRT and the process efficiency E (%) by:

$$\frac{1}{\theta_x} = Y(F:M)\frac{E}{100} - k_e$$

SRT values for activated sludge plants treating municipal wastewaters are typically in the range of 5-15 day with corresponding F:M values of 0.2-0.4/day. Increasing SRT increases the reactor concentration of biomass, which is often referred to as the MLSS. CAS processes operating at SRTs of around 8 days have an MLSS of 2.5 g/L, whereas one with a SRT of approximately 40 days might have a MLSS of 8-12 g/L. A low F:M ratio implies a high MLSS and a low sludge yield, such that increasing SRT is advantageous with respect to waste generation. This represents one of the key advantages of MBRs, and an analysis of data from the review by Stephenson et al. (2000) reveals that most MBRs, where SRT can be readily extended, operate at F:M ratios of < 0.12. On the other hand, high MLSS values are to some extent detrimental to process performance. Firstly, they would be expected to lead to an accumulation of inert compounds, reflected in a decrease in the MLVSS/MLSS ratio where MLVSS represents the organic fraction of the MLSS, though this does not appear to be the case in practice (Huang et al., 2001; Rosenberger et al., 2000). Secondly, high solids levels increase the propensity for clogging or "sludging" - the accumulation of solids in the membrane channels, an example of which can be observed in Figure 2-4.

Figure 2-4 - Typical sludging of an hollow fiber MBR

Lastly, and possibly most significantly, high MLSS levels reduce aeration efficiency. There have been a number of studies where the characteristics and performance of CAS and MBRs have been compared when these processes operated under the same conditions of HRT and SRT.

Le-Clech et al. (2003) observed sludge yields to be lower for an MBR than for a CAS process in their studies based on a skimmed milk-based analogue feed (0.22 vs. 0.28 and 0.18 vs. 0.24 for operation at 12 and 24 days SRT, respectively). This trend was repeated in the work reported by Smith et al. (2005), who also noted the greatest impact of the membrane separation to be on K_s. Given that K_s is inversely proportional to substrate affinity, the generally lower values of K_s in the case of an MBR suggest a greater biomass substrate affinity, and that the growth rate is less influenced by substrate concentration. Smith and co-workers proposed that this related to the difference in floc size, since the corresponding specific surface areas of the two biomasses at 30-day SRT were 0.098 m^2/g for the MBR and 0.0409 m^2/g for the conventional system, revealing that the MBR biomass provides over 230% more surface area at about the same MLSS concentration.

It is common practice to extend the SRT and HRT in the aeration basin to achieve the degradation of ammonia (NH_4-N). The effluent nitrogen concentration (N_e g/m^3) can be estimated by:

$$N_e = \frac{K_n(\mu_n + k_{e,n})}{\mu_{n,m} - k_{e,n} - \mu_n}$$

where $\mu_{n,m}$ is the maximum specific growth rate of nitrifying bacteria, K_n is the half saturation coefficient for nitrification, $k_{e,n}$ is the death rate coefficient for nitrifying bacteria and μ_n is the specific growth of nitrifying bacteria which can be found from:

$$\mu_n = \frac{1}{\theta_x}$$

Sludge production from nitrification is given by:

$$P_{x,aut} = \frac{QY_nNO_X}{1 + k_{e,n}\theta_x}$$

where Y_n is the nitrification sludge yield (g VSS/g NH_4-N) and NO_X is the concentration of NH_4-N that is oxidized (mg/L) to form nitrate (Lesjean et al., 2003). To calculate the NO_X, a nitrogen balance can be performed on the system:

$$NO_X = N - N_c + 0.12P_x$$

where N is the influent total Kjeldahl nitrogen concentration (TKN, mg/L). NO_X is used to determine P_x, NO_X can be estimated at the first attempt and iterated to find values for NO_X and $P_{x,\, aut}$.

Nitrifying bacteria function more slowly than carbon degraders such that, to accomplish nitrification, a longer HRT is required; nitrifiers are slower growing and need a longer SRT. An SRT of about 10 days is required to allow full growth of the nitrifying community (Huang, 2001). Fan et al. (1996) reported that total nitrification can be achieved in an MBR.

The removal of total nitrogen by biochemical means demands that oxidation of ammonia to nitrate takes place under aerobic conditions, and that nitrate reduction to nitrogen gas takes place under anoxic conditions (Yeo et al., 2007; Kim and Nakhla, 2009; Yeon et al., 2009). Both these processes demand that specific microorganisms prevail. The exact microorganisms responsible for denitrification (nitrate removal by biochemical reduction) are more varied – it is carried out by many different, phylogenetically-unrelated heterotrophs (Lousada-Ferreira et al., 2009; Min et al., 2008). The biological generation of nitrate from ammoniacal nitrogen and aerobic conditions, takes place in two distinct stages:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

Overall:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

Since the second step proceeds at a much faster rate than the first, nitrite does not accumulate in most bioreactors. However, since these microorganisms are autotrophic and thus rather slow growing, they demand relatively long SRTs to accumulate and provide close to complete nitrification (i.e. above 90% NH_4 removal). This presents another advantage of MBRs where long SRTs are readily attainable.

Denitrification takes place under anoxic conditions when oxidation of the organic carbon takes place using the nitrate ion, generating molecular nitrogen as the primary end product:

$$C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^-$$

where in this equation "$C_{10}H_{19}O_3N$" represents wastewater.

Nitrification relies on sufficient levels of carbon dioxide, ammonia and oxygen, the carbon dioxide providing carbon for cell growth of the autotrophs. Since nitrifiers are obligate aerobes, DO concentrations need to be 1.0-1.5 mg/L in suspended growth systems for their survival. Denitrification takes place when facultative microorganisms, which normally remove BOD under aerobic conditions, are able to convert nitrates to nitrogen gas under anoxic conditions. Denitrification requires a sufficient carbon source for the heterotrophic bacteria. This can be provided by the raw wastewater, which is why the nitrate-rich waste from the aerobic zone is recycled to mix with the raw wastewater (Iversen et al., 2008). Complete nitrification is common in full-scale MBR municipal installations, although, since it is temperature-sensitive, ammonia removal generally decreases below 10°C (Bacchin et al., 2006; Judd, 2010). Most full-scale MBR sewage treatment plants are also designed to achieve denitrification (Van der Marel et al., 2009; Van den Broek et al., 2010. Most wastewaters treated by biological processes are carbon limited, and hence phosphorus is not significantly removed (Lim et al., 2007). This applies as much to MBRs as to conventional plants. It appears that membrane separation offers little or no advantage regarding phosphorus removal (Yoon et al., 2006). Enhanced biological phosphate removal can be achieved by the addition of an anaerobic zone at the front of an activated sludge plant and returning nitrate-free sludge from the aerobic zone (Ahmed et al., 2007). P removal is more commonly achieved by dosing with chemicals, such as metal coagulants or lime, which can form sparingly soluble precipitates.

A summary of biological parameters for full scale MBRs is reported in Table 2-1.

Table 2-1 - Operating parameters of full scale MBR plants treating urban wastewater (Kraume et al., 2005)

	Unit	CAS	MBR	ZenoGem Milton, (US)	6 full scale MBRs	BIOSEP (France)
SRT	d	10-25	30	> 15	25-28	> 20
HRT	h	4-8	8	3	< 10	
SSML	kg m^{-3}	5		15-20	8-16	15
F_{CV}	kg m^{-3} d^{-1}	0.32-0.64	0.4-0.7	2.5	0.32-0.79	
F_{CO}	kg kg^{-1} d^{-1}	0.05		< 0.2	0.02-0.066	
η BOD_5	%	85-95	98-99	> 99	98	> 97.5
Effluent	mg/L	15		< 2	< 5	
η COD	%	94.5	99		96.1	97
Effluent	mg/L				< 25	
η TSS	%	60.9	99.9	> 99		99.8
Effluent	mg/L	10-15		< 2	0	
Turbidity	NTU			< 0.1		
η N_{tot}	%			> 96	92	98.6
Effluent	mg/L	< 13		< 2	< 10	0.4
η NH_4^+	%	98.9	99.2	<0.5 mg/L	< 1 mg/L	
η P_{tot}	%	88.5	96.6	> 99	86.5	
Effluent	mg/L	0.8-1		< 0.1	1	

From the table it can be inferred that the quality of CAS effluent is a very significant issue. Firstly, microbiological contamination of the effluent may be appear since there is no physical barrier between activated sludge and treated water. Also, there is a problem with specific compounds whose biodegradation depends on specialized microbial species. If such species have a slow growth rate they will be washed out with the excess sludge during the constant and fast sludge disposal rate (i.e., short SRT) of CAS treatment. As a consequence, specialized slow-growers may not develop in sufficient number to degrade efficiently some trace pollutants. Emerging contaminants in municipal wastewater and their fate in the environment have become an issue of importance for the legislators and decision-makers. Since the design of most municipal WWTPs does not allow operation at longer SRTs, they may not be suitable for degradation of some organic micropollutants. To overcome the limitations of conventional treatment with activated sludge, MBR technology can be successfully employed. While bacteria in activated sludge decompose and degrade organic matter from the wastewater, membrane separates them from the treated water, thus replacing the secondary settler used in CAS. The simple change from one physical separation technique to another leads to quite complex changes in the process characteristics. It affects the sludge characteristics in several ways. During CAS treatment, the bacterium present can survive in the bioreactor only in the form of flocs because the ones that do not settle are discharged with the treated water. Also, due to its short SRT, it is necessary for all microorganisms to grow fast or otherwise they will be washed out from the bioreactor. In other words, microbial population in CAS is selected among fast-growing and floc-forming species. On the contrary, in the case of MBR, the bacterial ability to settle and to grow fast is of negligible importance. MBR works at much longer SRTs (Table 2-1), which can be measured in months rather than days. In such conditions, slower growing species with the ability to decompose less-biodegradable compounds have the opportunity to proliferate. In other words, in MBR selection among microorganisms is primarily made by their capability to degrade the substrate, which is also the primary purpose of the treatment process.

Without demand for settling of the sludge, the F/M ratio can be set much lower, thus allowing operation at much higher MLSS concentrations, which consequently leads to higher volumetric efficiency of the process. Given the reduction in bioreactor volume, the elimination of secondary clarifiers and the elimination of granular media filters, MBR typically has a much smaller footprint relative to CAS, when achieving the same discharge limits. Due to this footprint reduction, other concerns such as esthetics and odors can be more easily addressed.

A low F/M ratio means that less substrate is available per unit of biomass. In this manner, the sludge production in the process is much lower, or does not occur at all. Very low sludge production in pilot MBR operations are reported, but it is often impractical for full-scale operations to keep F/M too low. The design of such plants would include very high MLSS concentrations that can promote membrane clogging, or large bioreactors, which contributes to the initial capital cost. Moreover, high MLSS concentration reduces aeration efficiency, which is possibly the most significant problem with maintenance of high MLSS concentration. Nevertheless, due to the low F/M ratio, there is a significant decrease of sludge production in MBR in comparison to CAS, which then decreases the cost of excess sludge handling.

2.1.2 Historical development of MBRs

The first membrane bioreactors were developed commercially by Dorr-Oliver in the late 1960s (Michael and Fikret, 2002), with application to ship-board sewage treatment (Fane et al., 2005). Other bench-scale membrane separation systems linked with an activated sludge process were reported at around the same time (Hardt et al., 1970; Smith et al., 1969). These systems were all based on what have come to be known as "sidestream" configurations (sMBR), as opposed to the now more commercially significant "immersed" configuration (iMBR). The Dorr-Oliver membrane sewage treatment (MST) process was based on fiat-sheet (FS) ultrafiltration (UF) membranes operated at what would now be considered excessive pressures (3.5 bar inlet pressure) and low fluxes (171/(m^2 h), or LMH), yielding mean permeabilities of less than 101/(m^2 h bar), or LMH/bar). Nonetheless, the Dorr-Oliver system succeeded in establishing the principle of coupling an activated sludge process with a membrane to concentrate simultaneously the biomass whilst generating a clarified, disinfected product. The system was marketed in Japan under license to Sanki Engineering, with some success up until the early 1990s. Developments were also underway in South Africa, which led to the commercialization of an anaerobic digester UF (ADUF) MBR by Weir Envig (Jons et al., 1999), for use on high-strength industrial wastewaters.
At around this time, from the late 1980s to early 1990s, other important commercial developments were taking place. In the USA, Thetford Systems were developing their Cycle-Let process, another sidestream process, for wastewater recycling duties. Zenon Environmental, a company formed in 1980, were developing an MBR system, which eventually led to the introduction of the first ZenoGem iMBR process in the early 1990s. The company acquired Thetford Systems in 1993. Meanwhile, in Japan, the government-instigated Aqua Renaissance program prompted the development of an FS-microfiltration iMBR by the agricultural machinery company Kubota. This subsequently underwent demonstration at pilot scale, first at Hiroshima in 1990 (0.025 MLD) and then at the company's own site at Sakai-Rinkai in 1992 (0.110 MLD). By the end of 1996, there were already 60 Kubota plants installed in Japan for night soil, domestic wastewater (i.e. sewage) and, latterly, industrial effluent treatment, providing a total installed capacity of 5.5 MLD. In the early 1990s, only one Kubota plant for sewage treatment

had been installed outside of Japan, this being the pilot plant at Kingston Seymour operated by Wessex Water in the UK. Within Japan, however, the Kubota process dominated the market in the 1990s, effectively displacing the older sidestream systems, such as that of Rhodia-Orelis (now Novasep Orelis). To this day, Kubota continues to dominate the Japanese membrane wastewater treatment market and also provides the largest number of MBRs worldwide, although around 86% of these are for flows of less than 0.2 MLD.

In the late 1980s, development of a hollow fibre (HF) UF iMBR was taking place both in Japan, with pioneering work by Kazuo Yamamoto and his co-workers (1989), and also in the US. By the early 1990s, the ZenoGem process had been patented (Ernst et al., 2007; Le-Clech, 2007), and the total installed capacity had reached 2.8 MLD from installations in North America. Zenon introduced its first immersed HF ZeeWeed module in 1993, this being the ZW145 (145 square feet), quickly followed by the ZW130 and 150 modules. These were in time superseded by the first of the ZW500 series in 1997. The company introduced the ZW500b, c and d modules in 1999, 2001 and 2003 respectively, the design changing to increase the overall process efficiency and cyclic aeration in 2000. Over this period, Kubota also developed products with improved overall energy efficiency, introducing a double-decker design in 2003.

As already stated, the cumulative capacity of both Zenon and Kubota has increased exponentially since the immersed products were first introduced, as shown in Figure 2-5.

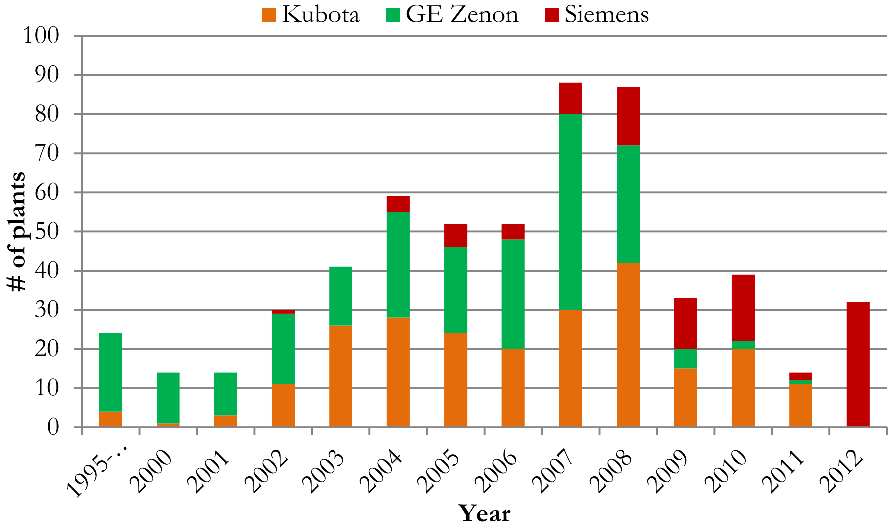

Figure 2-5 - Number of full-scale MBRs projects approved per year

These two systems dominate the MBR market today, with a very large number of small-scale Kubota systems and the largest MBR systems tending to be Zenon.

2.1.3 MBR Market

Of the many factors influencing the MBR market, which is represented in Figure 2-6, those that are generally acknowledged to be the main ones comprise:

(a) new, more stringent legislation affecting both sewage treatment and industrial effluent discharge;

(b) local water scarcity;

(c) the introduction of state incentives to encourage improvements in wastewater technology and particularly recycling;

(d) decreasing investment costs;

(e) increasing confidence in and acceptance of MBR technology.

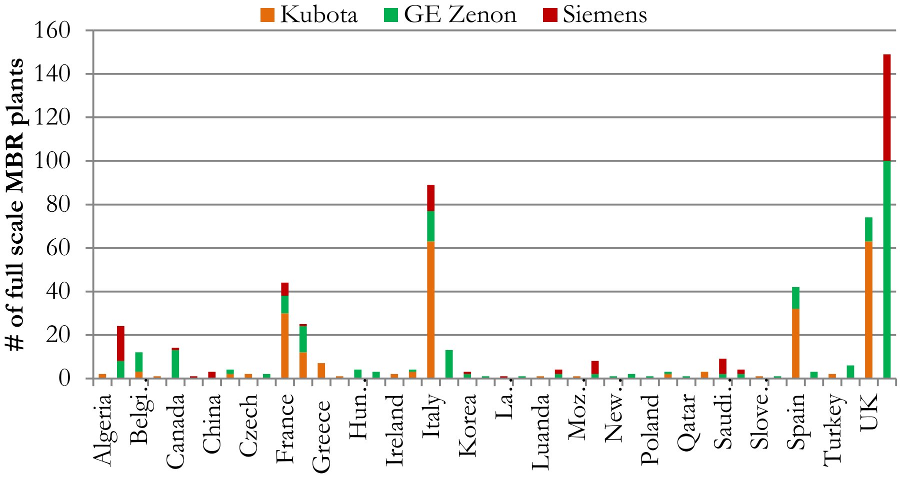

Figure 2-6 - Geographical distribution of MBR plants designed by three of the main membrane manufacturers worldwide

A thorough analysis of three among the main MBR producers worldwide (Zenon GE, Kubota, Siemens) is reported in the following figures, where geographical prominence is shown for each of the three companies.

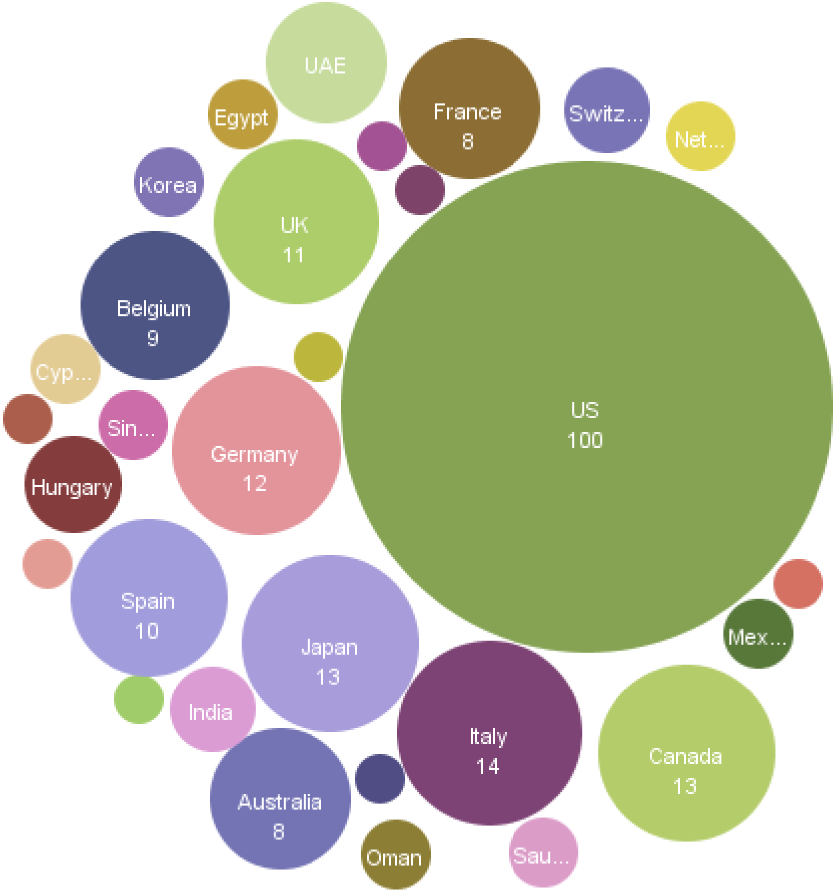

Figure 2-7 - Geographical distribution of Zenon GE MBR plants: evenly split across the main industrialized countries, apart from the US that has been bound to Zenon for decades

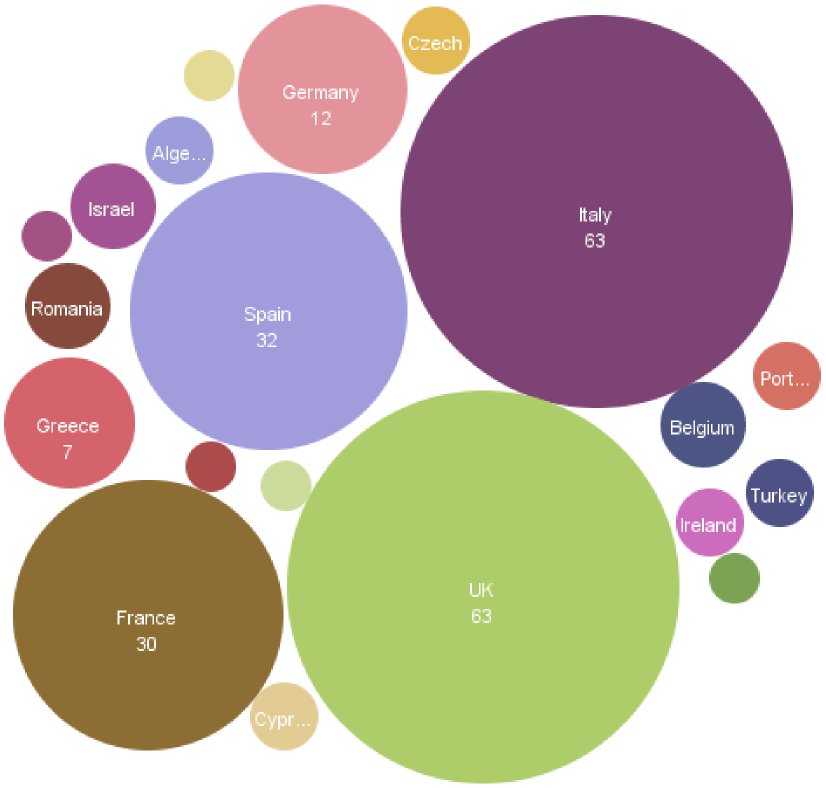

Figure 2-8 - Kubota plants worldwide: Italy and UK are the company stronghold in the EU

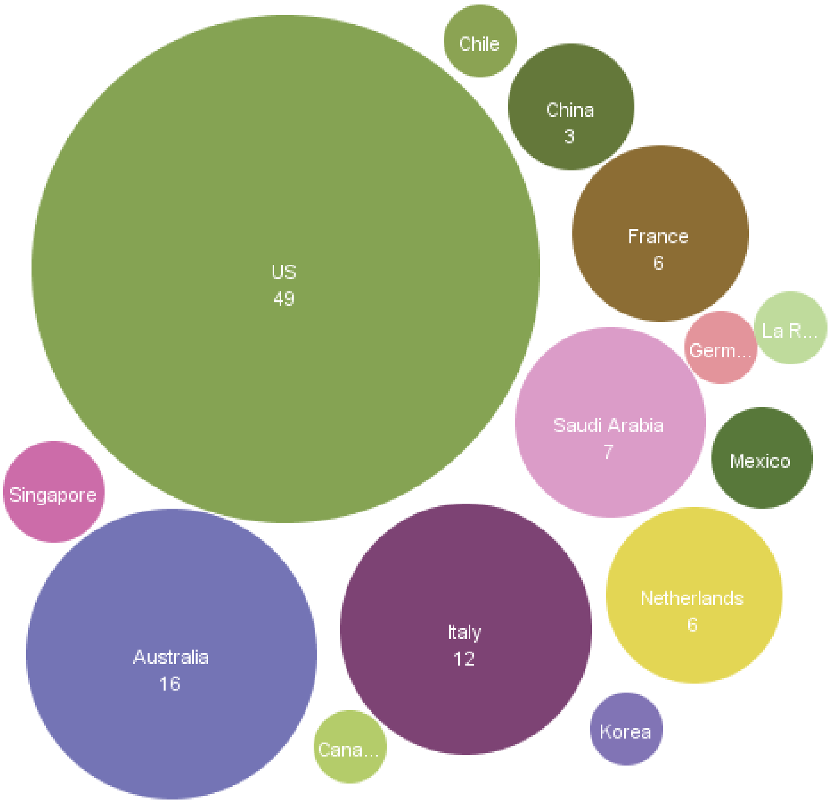

Figure 2-9 - Siemens MBR plants worldwide: its acquisition of Memcor boosted the company's presence in emerging markets such as Saudi Arabia and China

Legislation

There appears to be little doubt that the major driver in the MBR market today is legislation, since it enforces more stringent water quality outputs and water resource preservation globally, often through recycling, and therefore demands that organizations re-evaluate their existing technology in the light of the new requirements. A number of reuse and recycling initiatives have also been introduced to the same effect.

In the European Union pertinent legislation is manifested as a series of acts relating to water and wastewater, of which the most important with respect to MBRs are:

- The EC Bathing Water Directive (1976): This directive was designed to improve bathing water quality with respect to pathogenic micro-organism levels in Europe at selected localities and is currently under revision in order to both simplify and update it.
- The Urban Waste Water Treatment Directive (1995): The purpose of this directive, which was agreed in 1991, is to protect the environment from the negative effects of sewage discharges. Treatment levels were to be set taking into account the size of sewage discharges and the sensitivity of the waters into which the discharges were to be released (Judd, 2010).
- The Water Act: The Water Act, most recently amended and updated in 2003 (OFWAT, 2003), comprises three sections and relates to the abstraction and impounding of water resources, regulation of the water industry and a miscellaneous section.
- The Integrated Pollution Prevention and Control (IPPC) Directive (1996) which applies to the industrial sector and is intended to minimize pollution from industrial operations of all types, often requiring organizations to upgrade their technology to meet stringent requirements to receive a mandatory permit to continue operation. Obtaining a permit requires organizations to demonstrate their plant operates on the basis of the best available technique.
- The EU Landfill Directive: promulgated in 1999, its purpose is to encourage waste recycling and recovery and to reduce waste levels. The directive addresses the pollution of surface water, groundwater, soil and air, and of the global environment, including the greenhouse effect, as well as any resulting risk to human health, from the landfilling of waste, during the whole life cycle of the landfill (Judd, 2010).
- The EC Water Framework Directive: this came into effect in December 2000 and is the most substantial piece of EC water legislation to date (Judd, 2010). This very comprehensive directive integrates many other directives concerning water

> resources and discharges and requires that all inland and coastal waters reach "good status" by 2015.

In an attempt to reach the "fishable" and "swimmable" goal, the total maximum daily load (TMDL) program has been established. Section 303(d) of the CWA requires the establishment of a TMDL for all impaired waters. A TMDL specifies the maximum amount of a pollutant that a water body can receive and still meet water quality standards considering both point and non-point sources of pollution. The TMDL addresses each pollutant or pollutant class and control techniques based on both point and non-point sources, although most of the emphasis seems to be on non-point controls. MBRs thus offer the opportunity of a reduction in volume of point source discharges through recycling and improving the quality of point discharges to receiving waters. It is this that has formed part of the rationale for some very large MBRs recently installed or at the planning stage, such as the broad run water reclamation facility plant planned for Loudoun County in Virginia.

In the USA, individual states, and particularly those with significant water scarcity such as California and Florida, may adopt additional policies and guidelines within this legislative framework. The state of Georgia, for example, has implemented a water reuse initiative entitled 'Guidelines for Water Reclamation and Urban Water Reuse' (GDNR, 2006). The guidelines include wastewater treatment facilities, process control and treatment criteria, as well as system design, operation and monitoring requirements. California has introduced a series of state laws since the promulgation of the Federal Water Pollution Control Act, as amended in 1972. The most recent of these is the Water Code (Choi et al., 2002; Berman and Holenberg, 2005; Dong and Jiang 2009) which covers issues such as wastewater treatment plant classification and operator certification and on-site sewage treatment systems, amongst a whole raft of other issues. These are merely examples of pertinent legislation since a full review of all global legislation, regulations and guidelines is beyond the scope of this book. However, they give some indication of the regulatory environment in which MBR technology stakeholders are operating. There is also every reason to suppose that legislation will become more stringent in the future in response to ever depleting water resources and decreasing freshwater quality.

Incentives

Alongside legislative guidelines and regulations has been the emergence of a number of initiatives to incentivize the use of innovative and more efficient water technologies aimed at industrial and municipal organizations. These have an important impact on affordability and vary in amounts and nature (rebate, subsidy, tax concessions, etc.) according to national government and/or institutional/organizational policy but are all driven by the need to reduce freshwater demand.

In the UK in 2001, the HM Treasury launched a consultation on the Green Technology Challenge. The Green Technology Challenge is designed to speed up technological innovation and facilitate the diffusion of new environmental technologies into the market place (Judd, 2010). The initiative is intended to accompany tax credits previously available to SMEs to encourage research and development and to offer further tax relief on investment in environmentally-friendly technologies in the form of enhanced capital allowances (ECAs). Under the system water efficient technologies (e.g. those delivering environmental improvements such as reductions in water demand, more sustainable water use and improvements in water quality) are eligible for claiming ECAs. The tax incentive allow organizations to write off an increased proportion of its capital spending against its taxable profit over the period in which the investment is made. Similar tax incentives are offered to businesses in a number of other countries to encourage investment in environmentally-friendly and innovative technologies. In Australia, Canada, Finland, France, the Netherlands and Switzerland, this takes the form of accelerated depreciation for investment in equipment aimed at different forms of pollution. Denmark offers a subsidy-based scheme for investments directed towards energy-intensive sectors, and Japan also offers the option of a tax credit for the investment: from April 1998 to March 2004, suction filtration immersed membrane systems for MBRs were the object of "Taxation of Investment Promotion for Energy Supply Structure Reform", allowing a 7% income tax deduction for Japanese businesses. In the USA, state funding is also in place to encourage innovation in new water technology. The Clean Water State Revolving Fund (CWSRF) (which replaced the Construction Grants scheme and which is administered by the Office of Wastewater Management at the US Environmental Protection Agency) is the largest water quality funding source, focused on funding wastewater treatment systems, non-point source projects and watershed protection (Cote et al., 1997). The program provides funding for the construction of municipal wastewater facilities and implementation of non-point source pollution control and estuary protection projects. It has provided more than $4 billion annually in recent years to fund water quality protection projects for wastewater treatment, non-point source pollution control, and watershed and estuary management. In total, CWSRFs have funded over $ 52 billion, providing over 16700 low-interest loans to date (Drews et al., 2006). Other sources of funding for US projects are Water Quality Co-operative Agreements and the Water Pollution Control Program, amongst others. As with regulation on water use and discharge, individual states may have their own funding arrangements.

It is evident that governmental organizations are now offering incentives for investment in innovative water technology projects; as a result, MBR technology becomes more attractive in terms of affordability.

Having said this, the choice of technology is not normally stipulated by legislators, regulators or incentive schemes but may be inferred by the performance or quality standards set. The benefits of MBRs from the perspective of recycling is (a) their ability to produce a reasonably consistent quality of delivered water independent of variations in feedwater quality; (b) their relative reliability and (c) their small footprint.

Investment costs

Increasingly reliable and a greater choice of equipment, processes and expertise in membrane technology are available commercially for a range of applications, reducing unit costs by up to 30-fold since 1990 (Scannapieco et al., 2012). Future cost reductions are expected to arise from continued technical improvements and the economies of scale derived from a growing demand for membrane production (Lesjean et al., 2004). Costs of both membranes and processes appear to have decreased exponentially over the past 10-15 years, with whole life costs decreasing from $\$400/m^2$ in 1992 to below $\$ 50/m^2$ in 2005 (Kang et al., 2008). Such reductions have come about as a result of improvements in process design, improved O&M schedules and greater membrane life than that originally estimated. Having said this, although further cost reductions are expected in the future, there is some evidence that membrane purchase costs specifically are unlikely to decrease significantly unless standardization takes place in the same way as for reverse osmosis (RO). For RO technology, standardization of element dimensions has reduced the price of the membrane elements to below \$ 30/m^2 for most products from bulk suppliers.

Water scarcity

Even without legislation, local water resourcing problems can provide sufficient motivation for recycling in their own right. Water scarcity can be assessed simply through the ratio of total freshwater abstraction to total resources, and can be used to indicate the availability of water and the pressure on water resources. Water stress occurs when the demand for water exceeds the available amount during a certain period or when poor quality restricts its use. Areas with low rainfall and high population density or those where agricultural or industrial activities are intense are particularly prone to water stress (Koivunen et al., 2003). Changing global weather patterns aggravate the situation, in particular for those countries that are prone to drought conditions. Water stress induces deterioration of flesh water resources in terms of quantity (aquifer over-exploitation, dry rivers, etc.) and quality (eutrophication, organic matter pollution, saline intrusion, etc.). A widely used measure of water stress is the water exploitation index (WEI), the values of which represent the annual mean total demand for freshwater divided by the long-term average freshwater resource. It provides an indication of how the total water demand puts pressure on the water resource.

Data from the year 2000 indicate that four European countries (Cyprus, Italy, Malta and Spain) representing 18% of Europe's population, were considered to be water stressed. It is estimated that, in 1990, around 1.9 billion people lived in countries that used more than 20% of their potential water resources. By 2025, the total population living in such water-stressed countries is expected to increase to 5.1 billion, this figure rising further to 6.5 billion by 2085. On the other hand, climaterelated water stress is expected to reduce in some countries, for example, the USA and China, while in central America, the Middle East, southern Africa, North Africa, large areas of Europe and the Indian subcontinent, climate change is expected to adversely increase water stress by the 2020s. It is also predicted that 2.4 billion people will live in areas of extreme water stress (defined as using more than 40% of their available water resources) by 2025, 3.1 billion by 2050 and 3.6 billion by 2085; this is compared with a total population of 454 million in 1990 (Judd, 2010).

2.1.4 Membrane technology

A membrane as applied to water and wastewater treatment is simply a material that allows some physical or chemical components to pass more readily through it than others (Iversen et al., 2009). It is thus perm-selective, since it is more permeable to those constituents passing through it (which then become the permeate) than those which are rejected by it (which form the retentate). The degree of selectivity depends on the membrane pore size. The coarsest membrane, associated with microfiltration (MF), can reject particulate matter. The most selective membrane, associated with reverse osmosis (RO), can reject singly charged (i.e. monovalent) ions, such as sodium (Na^+) and chloride (Cl^-). Given that the hydraulic diameter of these ions is less than 1 nm, it stands to reason that the pores in an RO membrane are very small. Indeed, they are only visible using the most powerful of microscopes (Judd, 2010).

The four key membrane separation processes in which water forms the permeate product are RO, nanofiltration (NF), ultrafiltration (UF) and MF. Membranes themselves can thus be defined according to the type of separation duty to which they can be put, which then provides an indication of the pore size Ueda et al., 1997). The latter can be defined either in terms of the effective equivalent pore diameter, normally in µm, or the equivalent mass of the smallest molecule in daltons (Da) the membrane is capable of rejecting, where 1 Da represents the mass of a hydrogen atom. For UF membranes specifically the selectivity is thus defined by the molecular weight cut-off (MWCO) in daltons. For the key membrane processes identified, pressure is applied to force water through the membrane (Brepols et al., 2008). However, there are additional membrane processes in which the membrane is not necessarily used to retain the contaminants and allow the water to pass through, but can instead be used either to:

(a) selectively extract constituents (extractive) or
(b) introduce a component in the molecular form (diffusive).

Mature commercial membrane applications in water and wastewater treatment are limited to the pressure-driven processes and electrodialysis (ED), which can extract problem ions such as nitrate and those ions associated with hardness or salinity. Membrane technologies as applied to the municipal sector are predominantly pressure driven and, whilst the membrane selectivity and separation mechanism may vary from process to another, such processes all have the common elements of a purified permeate product and a concentrated retentate waste (Cui et al., 2003).

The rejection of contaminants ultimately places a fundamental constraint on all membrane processes. The rejected constituents in the retentate tend to accumulate at the membrane surface, producing various phenomena which lead to a reduction in the flow of water through the membrane (i.e. the flux) at a given transmembrane pressure (TMP), or conversely an increase in the TMP for a given flux (reducing the permeability, which is the ratio of flux to TMP). These phenomena are collectively referred to as fouling. Given that membrane fouling represents the main limitation to membrane process operation, it is unsurprising that the majority of membrane material and process research and development conducted is dedicated to its characterization and amelioration.

2.1.5 Membrane materials

There are mainly two different types of membrane material, these being polymeric and ceramic. Metallic membrane filters also exist, but these have very specific applications, which do not relate to membrane bioreactor (MBR) technology. The membrane material, to be made useful, must then be formed (or configured) in such a way as to allow water to pass through it (Pirbazari et al., 1996).

A number of different polymeric and ceramic materials are used to form membranes, but generally nearly always comprise a thin surface layer, which provides the required permselectivity on top of a more open, thicker porous support, which provides mechanical stability. A classic membrane is thus anisotropic in structure, having symmetry only in the plane orthogonal to the membrane surface. Polymeric membranes are also usually fabricated both to have a high surface porosity, or % total surface pore cross-sectional area, and narrow pore size distribution to provide as high a throughput and as selective a degree of rejection as possible. The membrane must also be mechanically strong (i.e. to have structural integrity). Lastly, the material will normally have some resistance to thermal and chemical attack, that is, extremes of temperature, pH and/or oxidant concentrations that normally arise when the membrane is chemically cleaned, and should ideally offer some resistance to fouling (Wu et al., 2008). Whilst, in principal, any polymer can be used to form a membrane, only a limited number of materials are suitable for the duty of membrane separation, the most common being:

- polyvinylidene difluoride (PVDF)
- polyethylsulphone (PES)
- polysulphone (PS)
- polyethylene (PE)
- polypropylene (PP)

All the above polymers can be formed, through specific manufacturing techniques, into membrane materials having desirable physical properties, and they each have reasonable chemical resistance (Drews, 2010). However, they are also hydrophobic, which makes the susceptible to fouling by hydrophobic matter in the bioreactor liquors they are filtering. This normally necessitates surface modification of the base material to produce a hydrophilic surface using such techniques as chemical oxidation, organic chemical reaction, plasma treatment or grafting (Liang et al., 2008). It is this element that, if at all, most distinguishes one membrane material product from another formed from the same base polymer. This modification process, the manufacturing method used to form the membrane from the polymer, most often PVDF for many MBR membranes, and the method for fabricating the membrane module from the membrane are all regarded as proprietary information by most suppliers (Pollice and Laera, 2005).

2.1.6 Membrane configurations

The configuration of the membrane, that is, its geometry and the way it is mounted and oriented in relation to the flow of water, is crucial in determining the overall process performance (Sethi et al., 2001). Other practical considerations concern the way in which the membrane elements, that is the individual discrete membrane units themselves, are

housed in "shells" to produce modules, the complete vessels through which the water flows (Pollice et al., 2004; Sagbo et al., 2008).
Ideally, the membrane should be configured so as to have:

(a) A high membrane area to module bulk volume ratio;
(b) A high degree of turbulence for mass transfer promotion on the feed side;
(c) A low energy expenditure per unit product water volume;
(d) A low cost per unit membrane area;
(e) A design that facilitates cleaning;
(f) A design that permits modularization.

All membrane module designs, by definition, permit modularization (f), and this presents one of the attractive features of membrane processes per se. This also means that membrane processes provide little economy of scale with respect to membrane costs, since these are directly proportional to the membrane area, which relates directly to the flow. However, some of the remaining listed characteristics are mutually exclusive. For example, promoting turbulence (b) results in an increase in the energy expenditure (c).
Direct mechanical cleaning of the membrane (e) is only possible on comparatively low area:volume units (a). Such module designs increase the total cost per unit membrane area (d), but are inevitable given that cleaning is of fundamental importance in MBR processes where the solids and foulant loading on the membrane from the bioreactor liquor is very high. Finally, it is not possible to produce a high-membrane area to module bulk volume ratio without producing a unit having narrow retentate flow channels, which will then adversely affect turbulence promotion and ease of cleaning. There are six principal configurations currently employed in membrane processes, which all have various practical benefits and limitations. The configurations are based on either a planar or cylindrical geometry and comprise:

1. plate-and-flame/flat sheet	(FS)
2. hollow fibre	(HF)
3. (multi)tubular	(MT)
4. capillary tube	(CT)
5. pleated filter cartridge	(FC)
6. spiral-wound	(sw)

Of the above configurations, only the first three are suited to MBR technologies, principally for the reasons outlined previously: the modules must permit turbulence promotion, cleaning or, preferably, both (Mohammadi et al., 2003). Turbulence can arise through either the feedwater or an air/water mixture along the surface of the membrane to support the passage of permeate through it. This crossflow process is broadly used in many membrane applications, and its efficacy escalates with increasing membrane interstitial distance (Macomber et al., 2005; Judd, 2010).

Because the MT module operates with flow passing from inside to outside the tube ("lumen-side" to "shell-side"), whereas the HF operates outside-to-in, the interstitial distance can be defined by:

- The tube diameter for a MT;
- The distance between the filaments for an HE;
- The channel width for an FS.

The membrane packing density of the HF therefore becomes crucial, since an increased packing density could reduce the interstitial gap to the point where clogging may arise onto membrane pores. CT modules, which are, to all intents and purposes, HF modules with reversed flow, are too narrow in diameter to be used for MBR applications, as they would be at high risk of clogging (Leiknes et al., 2006).

Physical cleaning is most simply affected by reversing the flow (i.e. backwashing), at a rate 2-3 times higher than the forward flow, back through the membrane to remove some of the fouling layer on the retentate side (Drews, 2010). For this to be feasible, the membrane must have sufficient inherent integrity to withstand the hydraulic stress imparted. In other words, the membrane must be strong enough not to break or buckle when the flow is reversed (Panglish and Gimbel, 2004). This generally limits backwashing of polymeric membranes to those configured as capillary tubes or HFs. At low filament diameters the membranes have a high enough wall thickness: filament diameter ratio to have the inherent strength to withstand stresses imposed by flow reversal (McAdam et al., 2005).

The performance of the MBR process is also determined by the configuration of the membranes, which depends on the geometry (planar or cylindrical), mounting and orientation in relation to the flow of water. Membranes can be immersed into the oxidation tank of the WWTP or can be located in a different element, directly linked to the tank. The feed to the oxidation tank is pressurized and circulated through the tank module with the use of a pump. A valve assists in the accumulation of the wastewater constituents on the membranes. Flocs and dispersed microorganisms are kept in the MBR system to biodegrade and transform pollutants.

In general, membrane processes include microfiltration or MF (0.08-2.0 μm), ultrafiltration or UF (0.005-0.2 μm), nanofiltration or NF (0.001-0.01 μm), reverse osmosis (0.001-0.0001 μm), dialysis and electrodialysis (Judd, 2010). Concerning MBRs, small organic monomers such as pharmaceuticals, pesticides and herbicides fall under the 10-4 to 10-2 μm pore size of MBR and thus can be removed by ultrafiltration (UF) while bacteria have a size of 10 to 100 μm can be removed with microfiltration (MF) (Metcalf and Eddy, 2003).

Dialysis involves the transport of molecules in water down a concentration gradient, while electrodialysis uses the active transport of molecules with the use of an electromotive force and an ion-selective membrane to achieve ionic species separation (Judd, 2010). In reverse osmosis and NF small particles are rejected by water layer while ionic species cross the membrane (Metcalf and Eddy, 2003). The range of actual wastewater filtration sizes lies in the range of 0.0001 μm to 1 μm, in order to include dissolved wastewater constituents and includes the process of reverse osmosis up to the range of microfiltration.

The choice of membrane and system configuration is optimized when the factors of minimizing clogging and deterioration are considered. The flat sheet (FS) has two types, the composite and asymmetric. Asymmetric membranes have a very thin layer (<1 μm) and a thick porous layer (100 μm) adding support and high water flux.

The constituent material of MBR can be ceramic, polymeric or organic. The main materials of membranes include polypropylene, cellulose acetate, aromatic polyamides and thin-film composite (Judd, 2010). Composite membranes have thin cellulose acetate bonding, polyamide or another active layer (mainly 0.15-0.25 µm) and a thicker porous substrate that provides stability.

As MBRs show a better behavior in the removal of pharmaceuticals than CAS treatments, their implementation should be encouraged on a wide basis. This would benefit water treatment and the environment. Solids concentration is higher in MBRs than in CAS processes, so biological activity and concentration of filters has to be high to serve the biomass. Physical separation removes both biodegradable and non-biodegradable compounds, therefore limiting the occurrence of biorecalcitrant compounds in the WWTP effluent. Moreover, a reduced footprint is considered another advantage of MBRs, because their compact design uses 50 to 80% less space than conventional treatment plants (Wedi, 2003; Judd, 2010). Lower operational costs may be generated by MBRs when compared to CAS processes, which may increase for larger tanks, along with reduced need of workforce, as automation is enhanced in MBRs. The organic load collected from the MBR can also be converted to biosolids that can be used to produce energy, such as methane in digesters, or can be burned to produce other forms of thermal energy. As a result, costs on energy and aeration are saved, in combination with ecological benefits.

2.2 FOULING IN MBRS

Fouling in its simple form is the coverage of the membrane surface (external and/or internal) by deposits, which adsorb or simply accumulate during regular filtration. According to a widely used bibliographic database, an increasing number of publications is dealing with fouling in MBRs, for a total of roughly 1700 papers on MBRs until 2011, of which more than 60% coped with the fouling issue (Santos, 2011).

However, the term "fouling" is often used to combine all those phenomena that might lead to a loss in permeability. Such a loss results in larger required membrane surfaces, higher applied pressures or shear rates that both result in higher energy expenditure (Chisti et al., 1988). Permeability loss, though, can also be caused by clogging or sludging of the module. This results from the local breakdown of crossflow conditions and the subsequent dewatering of the biomass, which leaves a solid deposit in the voids of the modules (Vela et al., 2008; Menniti et al., 2009).

As showed in Figure 2-10, several factors might play a role in the development of a fouling layer in MBRs, some of them directly depending on the feed, while others being related to the MBR unit itself. Clearly, the membrane porosity – which lies in the range of the micro- or ultrafiltration – determines the fraction of solids allowed to pass the physical barrier, and therefore the fraction that will likely produce the fouling phenomenon.

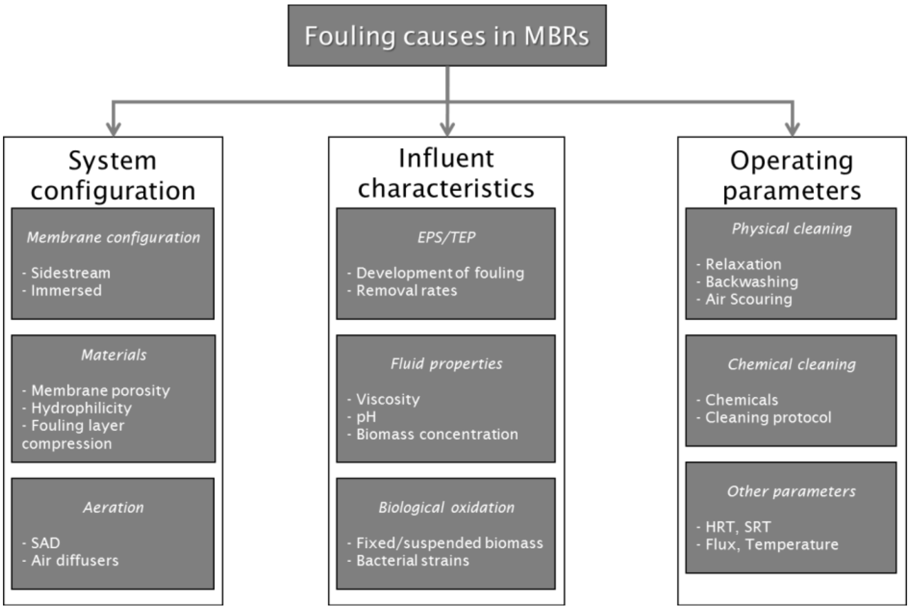

Figure 2-10 - Elements affecting MBR fouling behavior and control

Being deposits brought to the membrane mainly by convective transport, fouling rate depends on the velocity orthogonal to the membrane, namely the permeate flux (Moreau et al., 2009). This results in a pure optimization problem: at higher flux, capital costs decrease while operation and maintenance costs increase (Scannapieco et al., 2012). No doubts that if the correlation between fouling rate and flux were known, the optimization could be performed. Unfortunately, the rate of fouling depends on several other parameters. Therefore, in the existing literature there is a lack of fundamental understanding of relationship between fouling and flux in MBRs (Li et al., 2006).

Due to its economic impact, fouling has been a major issue in membrane separation – and particularly MBR research – for more than a decade with a steady increase in research activities. Approximately 30% of all MBR literature deal with fouling (Scannapieco et al., 2012), although unfortunately in contrast to the multitude of papers on lab or pilot-scale studies, there are very few full-scale investigations on fouling in MBRs (Judd, 2010).

In literature, several definitions of fouling can be found. In general, the term reversible fouling refers to fouling that can be removed by physical means such as backwashing or relaxation, whereas irreversible fouling refers to fouling that can only be removed by chemical cleaning (Ye et al., 2005; Drews, 2010). The definition of reversible fouling is due to the deposition of material on the membrane that can be removed through relaxation or backwashing. Once these methods have taken place, there is an amount of fouling that is not removed, also called irreversible fouling, that can be controlled only through chemical cleanings. What is left after chemical cleanings, commonly known as irrecoverable fouling, cannot be removed at all and occurs over long operation periods. Since people involved in MBR management need to cope with fouling control, several attempts have been made to correlate permeability decline with biomass concentration (Judd, 2010; Chang et al., 2002; Le Clech et al., 2003), floc size and – more recently – concentration of extracellular polymeric substances (EPS) or soluble microbial products (SMP) (Lesjean et al., 2004). Nevertheless, due to the complexity of the biological system and the lack of methods, available results are often contradictory (Drews et al., 2010).

Fouling phenomena occur over the membrane surface, therefore the configuration of the MBR, basically its geometry and the way it is oriented in relation to the flow, is critical in determining the overall process performance (Foley et al., 1992).

Membrane fouling results then from interaction between the membrane material and the compounds in the liquor. The latter include substrate components, cells, cell debris, and microbial metabolites. Consequently, although many studies of membrane fouling have been published (Drews, 2010), the varied range of operating conditions and feedwater matrices employed as well as the limited information reported on the biomass composition have made it difficult to establish any generic behavior pertaining to membrane fouling in MBRs specifically. Provided that MBR fouling represents the main limitation to membrane process operation (Chaize and Huyard, 1991; Drews, 2010), it is unsurprising that the majority of research in membrane material and process optimization is dedicated to its characterization and amelioration (Judd, 2010).

Fouling in MBRs can take place through a number of physicochemical and biological mechanisms, which are all related to increased deposition of solid material onto the membrane surface and in the membrane pores. In MBRs, as in many other membrane filtration processes, it is the balance between the flux and the physical or chemical cleaning which ultimately determines the extent to which fouling is successfully suppressed. Ultimately, fouling can be reduced by two methods: promoting turbulence and reducing flux (Rosenberger et al., 2005). In sMBRs, turbulence can be enhanced by increasing the crossflow velocity, whereas for an iMBR this can reasonably be achieved by enhancing the aeration. Ideal hydrodynamic conditions can be promoted also through passing either the wastewater or an air/water mixture beside the membrane surface to aid the passage of permeate through it (Nywening and Zhou, 2009).

Relaxation processes were introduced as to limit fouling formation (Lyko et al., 2007; Bracklow et al., 2008); relaxation is based on a dramatic reduction of the TMP for a short amount of time, leading to a substantial reduction of the stress field over the membrane (Judd, 2010).

The rejection of contaminants is a fundamental constraint on every membrane process. On one hand, wastewater treatment plants managers are interested in higher removal efficiencies regarding macropollutants; on the other hand, the more is blocked by the membrane, the more that membrane is fouled (Cote et al., 1998).

Regarding macropollutants removal, MBR systems can remove COD efficiently, as largely shown in literature (Yun et al., 2006; Zator et al., 2006; Drews, 2010) with overall organic degradation efficiencies in MBR higher than 85% in municipal wastewater treatment plants. This high removal efficiency implies that in the membrane bioreactor system, organic matter can be degraded at high rates, thanks to higher biomass concentrations and physical removal through membrane filtration that plays a major role in maintaining stable organic removal efficiency (Lee et al., 2007).

Total Kjeldahl Nitrogen removal efficiencies are high (Hwang et al., 2008), and this implies that the removal of nitrogen could be mostly due to the action of simultaneous nitrification and denitrification happening in the MBR. In addition, nitrogen compounds in the effluent appear mostly in the form of nitrate, therefore a complete nitrification process is achieved in MBRs (Hughes et al., 2007).

Consequently, MBRs are an attractive option for the wastewater treatment. However, membrane fouling in MBR is considered as a major limitation to faster commercialization of MBR technology due to the way it affects system performance (Chen et al., 2001). Thus, membrane fouling models that can accurately depict the propensity of fouling rates are valuable for the design and control of MBR systems (Judd, 2010).

As widely known, the rejection of pollutants puts a constraint on membrane processes (Eckstein et al., 1977). Rejected pollutants tend to accumulate on the membrane surface causing fouling phenomena leading to a reduction in the flow of water through the membrane at a given pressure (Judd, 2010). It has to be noted that higher removal efficiencies of membranes mean more blocking and accumulation of molecules on the membranes, and as a result more fouling (Chung et al., 2006). Therefore, the pressure builds up on the feed side and the flux through the membrane decreases. The rejection of pollutants by membranes eventually decreases as well (Santos et al., 2011). When that point is attained, the membrane modules are backwashed to remove fouling material, chemically cleaned and serviced to be reused, or are alternatively replaced (Franck and Belfort, 2003).

The main drawback of MBR technology in comparison to CAS treatments still is its high cost. While membrane module costs have decreased dramatically over the last years leading to a decrease in capital costs, membrane fouling abatement leads to elevated energy demands and has become the main contribution to overall MBR operating costs. Fouling affects these in a number of ways as listed below.

a) Decreased plant productivity/permeate yield due to:

    - filtration breaks and backwash: To remove the deposit layer, backwashing from the permeate side (hollow fibre modules) or relaxation (flat sheet modules) are commonly applied for approx. 15–60 s every 3–12 min of filtration (Judd, 2010; Kraume et al., 2005; Lyko et al., 2008);

  - frequent cleanings (maintenance cleanings approx. every 2–7 d, main cleanings once or twice a year (Drews, 2010). This also leads to environmental hazards through the formation of chemical cleaning by-products such as adsorbable organic halogens (AOX).

b) Damaging, inefficient or late chemical cleaning, which might reduce the modules' lifespan and result in higher replacement costs (Essemiani et al., 2001).
c) High energy requirement for aeration: with up to 70% of the total energy costs (Ang et al., 2006; Verrecht et al., 2008; Drews, 2010), membrane aeration is the biggest contribution to operating costs (Drews, 2010). From 10 years of experience of operating a full-scale MBR, it was found that only in 10% of the operational time, i.e. during peak loads, the supplied energy is optimally used (Di Trapani et al., 2011). This shows a large optimization potential.

Several attempts have been made to correlate permeability decline with biomass concentration (Chang et al., 2002; Le-Clech et al., 2003), floc size, sludge rheology, and concentration of bound or suspended EPS. Still, due to the complexity of the biological system and the lack of methods and terminology standardization, these are inconsistent and often contradictory.

2.2.1 Critical flux

The critical flux concept was originally presented by Field et al. (1995). These authors stated that: "The critical flux hypothesis for microfiltration/ultrafiltration processes is that on start-up there exists a flux below which a decline of flux with time does not occur; above it, fouling is observed". Two distinct forms of the concept have been defined. In the strong form, the flux obtained during sub-critical flux is equated to the clean water flux measured under the same conditions. However, clean water fluxes are rarely attained for most real feedwaters due to irreversible adsorption of some solutes. In the alternative weak form, the sub-critical flux is the flux rapidly established and maintained during start-up of filtration, but does not necessarily equate to the clean water flux (Lesage et al., 2005). Alternatively, stable filtration operation, that is, constant permeability for an extended time period, has been defined as sub-critical operation even when preceded by an initial decline in flux (Fane, 2005). Such conditions would be expected to lead to lower critical flux values than those obtained for constant permeability operation, however, since an initial permeability decline implies foulant deposition. A number of slightly different definitions of sub-critical flux operation have been proposed, largely depending on the method employed. The most microscopically precise definition equates the critical flux to that flux below which no deposition of colloidal matter takes place. Li et al. (1998) equated critical flux to the lift velocity as defined by the lateral migration theory of Green and Belfort (1980). This rigorous definition is difficult to apply because of the relative complexity of the determination of the lift velocity, particularly for heterogeneous matrices. On the other hand, experimental determination of critical flux by direct observation of material deposition onto the membrane has been conducted using model homodispersed suspensions of polystyrene latex particles (Li et al., 1998), and some authors have also used mass balance determinations (Yeom et al., 2005).

Given the limitations of applying particle hydrodynamics to the identification of the critical flux in real systems, recourse generally has to be made to experimental determination (Harmant and Aimar, 1996). By plotting flux against the TMP it is possible to observe the transition between the linearly pressure-dependent flux and the onset of fouling, where deviation from linearity commences (Jarusutthirak et al., 2002). The flux at this transition has been termed "secondary critical flux" (Bouhabila et al., 2001) and, more recently, the concept of "sustainable flux" has been introduced, defined as the flux for which the TMP increases gradually at an acceptable rate, such that chemical cleaning is not necessary (Ng and Hermanowicz, 2005).

Whilst potentially useful in providing a guide value for the appropriate operating flux, the absolute value of the critical flux obtained is dependent on the exact method employed for its determination and, specifically, the rate at which the flux is varied with time. A common practice is to incrementally increase the flux for a fixed duration for each increment, giving a stable TMP at low flux but an ever-increasing rate of

TMP increase at higher fluxes (Tay et al., 2007; Thiemig et al., 2008). This flux-step method defines the highest flux for which TMP remains stable as the critical flux. This method is preferred over the corresponding TMP-step method since the former provides a better control of the flow of material deposition on the membrane surface, as the convective flow of solute towards the membrane is constant during the run (Busch et al., 2007). No single protocol has been agreed for critical flux measurement, making comparison of reported data difficult, though a practical method based on a threshold permeability change has been proposed by Le-Clech et al. (2003). Within the last few years, it has become apparent from bench- and pilot-scale studies that irreversible fouling of MBR membranes can take place at operation well below the critical flux. Pertinent studies have been summarized by Pollice et al. (2005).

Sub-critical flux fouling appears to be characterized by a sudden discontinuity of the TMP at very low flux operation after some extended time period (Ognier et al., 2004; Wicaksana et al., 2009) and a steady neo-exponential increase at fluxes closer to the notional critical flux.

2.2.2 Biological issues in MBRs

Biological treatment relies on conversion of organic and inorganic matter into innocuous products by microorganisms and, as such, the biological community must be healthy and sustainable (Van de Ven et al., 2008; Van den Brink et al., 2009). Higher forms of microorganisms such as protozoa and rotifers play crucial roles in consuming suspended organic matter and controlling sludge concentration by scavenging bacteria (Choi et al., 2004). Larger biological species such as nematode worms and insect larvae may contribute to the consumption of particulate organic matter. There is evidence to suggest that higher organisms, protozoa, filamentous organisms, nematodes and ciliates, are present at lower concentrations in MBRs than in conventional activated sludge systems (Cicek et al., 2001; Rosenberger et al., 2002). However, higher concentrations of protozoa, particularly flagellates and free ciliates, have been reported for MBRs compared with an activated sludge operating at the same SRT (Miyoshi et al., 2009). These experiments were performed on a system with long HRT (20-74 h) hence the shorter HRT associated with MBRs may be responsible for the absence of protozoa in other studies. Predatory organisms have a negative effect on nitrification (Li et al., 1998) and overgrowth of protozoa have been shown to create a complete breakdown of nitrification (Barker and Dold, 1996; Wang and Waite, 2008). This grazing in activated sludge is accounted for in the death coefficient (k_e), and recent research suggests that this effect has a greater impact on sludge concentration than previously thought in an activated sludge system (van Loosdrecht and Henze, 1999).

In contrast, the sludge concentration in an MBR is limited by the energy provided and cell decay (Low and Chase, 1999; Schaller et al., 2006). Higher organisms, such as nocardia, have been shown to develop in full-scale MBRs and produce significant foaming problems. Conditions are created in an MBR by allowing the sludge to accumulate to a maximum biomass concentration where all of the energy available is used for cell maintenance (Knoblock et al., 1994; Smith et al., 2006). The high sludge concentration compared to the food available creates an environment where bacteria are facing starvation conditions so the bacteria are not in a physiological state for cell growth (Muller et al., 1995). Oxygen uptake rates in an MBR system compared with a conventional activated sludge system are lower, indicating that the MBR is carbon rather than oxygen limited (Rosenberger et al., 2002). Even if the cells in an MBR system are not growing, new bacteria are constantly being introduced with the influent wastewater; since no grazing organisms exist, there must be cell decay to keep the biomass concentration constant (Koseoglu et al., 2008).

The microbial community in any biological system comprises a large number of different bacterial species. In both an MBR and activated sludge system, the dominant group of bacteria have been shown to be [3-subclass Proteobacteria (Rosenberger et al., 2000; Sofia et al., 2004); all currently characterized ammonia oxidizers belong to this group. Although these bacteria remained dominant in an MBR, a higher proportion of other bacteria (52-62%) were recorded in these studies suggesting that the long SRT shifted the microbial population away from Proteobacteria-[3 (Sofia et al., 2004). Nitrosomonas and Nitrosospira are the autotrophic ammonia-oxidizing bacteria found in activated sludge, and Nitrobacter and Nitrospira the nitrite-oxidizing bacteria, and it is thus between these groups that the nitrification process is carried out (Laspidou and Rittman, 2002). Sofia et al. (2004) found the predominant nitrifiers were Nitrosospira and Nitrospira, whilst Rosenbergersofia et al. (2002) showed no Nitrosomonas or Nitrobacter or Nitrosospira to be found in membrane-filtered sludge. This implies that the ammonia-oxidizing bacteria are system-specific and that Nitrospira are responsible for the reduction of nitrite. Nitrifying autotrophs are known to be slow-growing bacteria. The long SRTs available in an MBR system are thus accepted as being highly advantageous for nitrification (Haberkamp et al., 2007).

Microorganisms can be classified according to the redox conditions in which they prevail, and hence the process type, and their energy requirements (Mehrez et al., 2007).

Heterotrophs use organic carbon as an energy source and for synthesis of more cellular material, and are responsible for BOD removal and denitrification. Autotrophs use inorganic reactions to derive energy, for example, oxidation of iron (II) to iron (III) or hydrogen to water, and obtain assimilable material from an inorganic source (such as carbon from carbon dioxide) to carry out such processes as nitrification, sulphate reduction and anaerobic methane formation. Autotrophs are generally less efficient at energy gathering than heterotrophs and therefore grow more slowly.

Microbial growth relies on appropriate conditions of total dissolved solids (TDS) concentration, pH and temperature (Jofre et al., 1995). Most microorganisms can only function in relatively dilute solutions, around neutral pH and at ambient temperature, though some can grow under extreme conditions: Thiobacillus growth is optimum at pH 1.5-2.0.

Some MBRs are based on growth of specific cultures, such as for nitrification, or recalcitrant organics biodegradation in extractive MBRs.

Classification of microorganisms according to the temperature at which they are most active provides the terms psychrophilic, mesophilic and thermophilic for optimum growth temperatures of 15, 35 and 55 °C respectively (Ngo et al., 2008). While most aerobic biological processes are operated at ambient temperatures, the microorganisms usually have mesophilic temperature optima, such that pumping operations in sMBRs can provide additional benefit in raising the reactor temperature to both increase biotreatment efficacy and reduce liquid viscosity (Van der Gast et al., 2006). Few examples exist of MBRs operating under thermophilic conditions, though this mode appears to offer some promise for treatment of heavy COD loads and/or recalcitrant organic matter.

2.2.3 Main foulants

MBR biomass consists of variable amounts of particulate, colloidal and dissolved fractions, all of which contain potential foulants. After initially MLSS concentration was thought to govern the rate of fouling, the focus has quickly turned to slimy and sticky substances, which can be bound to the flocs or freely suspended (Joss et al., 2009).

These groups of compounds are mostly termed EPS when they are bound to the flocs or soluble microbial products (SMP) when freely suspended in the supernatant. Recently, the terms biopolymers or biopolymeric clusters (BPC) have also come into use (Wang et al., 2008). Another group which until recently had only been studied in the formation of biofilms in seawater environments (Song et al., 2003; Berman and Holenberg, 2005) are the so-called transparent exopolymer particles (TEP). By definition, all these groups of compounds are produced and excreted by microorganisms (Horan, 1990). However, what is analyzed as EPS, SMP, BPC or TEP by commonly agreed on methods is not necessarily of microbial origin but can also be terrestrial or man-made (Drews, 2010). Depending on the applied assays, these groups are not distinct but overlap. Unfortunately, the location of the fouling relevant fraction is still unknown, so are the conditions that shift it to different locations. Especially since a linear relationship between fouling rate (increase of temperature corrected filtration resistance over time) and polysaccharide (PS) concentration in the sludge supernatant was observed (Lesjean et al., 2004; Rosenberger et al., 2006), attention has been focused on soluble EPS or SMP. EPS and SMP consist of polysaccharides (PS), proteins, lipids, nucleic acids, etc. which can originate from cell lysis, microbial metabolites or unmetabolized wastewater components (Judd, 2010). Usually, PS and proteins are assumed to be the major fractions that contribute to fouling (Ndinisa et al., 2006; Drews et al., 2010). Thus, the determination of EPS or SMP concentration relies almost exclusively on PS and protein measurements. The typically used photometric Dubois (Dubois et al., 1956), Lowry (Lowry et al., 1951) and Bradford (Bradford, 1974) assays for SMP and EPS analysis, the extraction methods to measure bound EPS and also the sample preparation methods to obtain representative sludge supernatants have been exhaustively described and discussed in literature, so only a few additional aspects shall be pointed out here.

Polysaccharides: Given the typical analysis, carbohydrates is a more appropriate term because the assay is not limited to polysaccharides but also detects mono- and oligosaccharides. The presence of nitrate and nitrite in the sample has been found to impair the Dubois assay and to lead to elevated values. Therefore, both compounds should routinely be measured in each sample to enable a correction of the measured carbohydrates concentration (Drews, 2010).

Proteins: Since the Lowry assay is not only protein specific but also responds to humic substances, the modified method by Frølund et al. (1996) is often used. In certain regions like Berlin where samples have a high ion and specifically calcium content, this modified method, however, cannot be employed because precipitation occurs during analyses, which leads to higher absorption. This limits the comparability of results obtained worldwide even further (She et al., 2009).

Instead of analyzing these fractions, some authors measure DOC or TOC in the supernatant and the extract (Dong and Jiang, 2009) or even COD (Jiang et al., 2008) to report SMP and EPS concentrations. Lyko et al. (2008) propose DOC as an alternative to complex, tedious and costly SMP/EPS measurements to characterize the biomass. Wang and Li (2008) argue that any TOC compounds that pass the membrane can only be SMP and define the difference in TOC concentration between permeate and sludge supernatant as biopolymer clusters (BPC). These BPC are too large to pass the membrane but are biodegradable and thus were apparently formed by adsorption and affinity clustering of SMP. In trials with a lab-scale MBR fed on synthetic wastewater, they found a weak correlation between BPC concentration and TMP as a function of productivity (i.e., permeate volume over membrane surface).

With such photometric methods or TOC measurements, only surrogate concentrations of EPS, SMP, carbohydrates, proteins or related compounds can be determined, however, no information on individual constituents or their properties can be obtained with these approaches. In other words, two samples with equal net carbohydrate, protein or TOC concentration can exhibit largely different behavior.
A method that detects a more specific fraction of polysaccharides is the staining of transparent exopolymer particles (TEP) whose existence in

seawater was described by Alldredge et al. (1993). The staining protocol was established for dilute systems by Passow and Alldredge (1995), developed further by Arruda et al. (2004) and adapted to activated sludge systems by de la Torre et al. (2008).

Berman and Holenberg (2005) proposed that TEP is a prime factor leading to biofilm growth on RO membrane surfaces, and suggested measuring TEP concentrations to determine the efficiency of prefiltration arrays upstream from membranes in seawater membrane desalination systems (de la Torre et al., 2009). TEP are measured by staining with alcian blue, a cationic dye which binds to acidic mucopolysaccharides. The specific detection of this fraction, which has an acidic and hydrophobic character, might prove to be interesting in MBR fouling, too (Harscoat et al., 1999).

In addition, the TEP staining method has several advantages over the Dubois method: It is simpler and faster, accurate and reliable, the dye is non-toxic and no strong acids are used, so that there are no hazardous residues after the test. Besides, no special correction is needed for the presence of nitrate and nitrite (de la Torre et al., 2008).

A parameter which gives an indication of aromaticity or hydrophobicity is the specific UV absorbance (SUVA) which is calculated from the absorbance at 254 nm divided by the DOC concentration. Low hydrophobicity of flocs or bound EPS is typically assumed to cause higher fouling due to floc deterioration and stronger interactions with the typically hydrophilic membrane. The latter becomes less important as the surface chemistry is quickly masked during the process by adsorption and cake formation (Drews, 2010).

Wang et al. (2009) use the oxidation state of organics (calculated from TOC and COD measurements) as a surrogate to estimate the main EPS or SMP components (Remy et al., 2009; Rochex et al., 2008). Several chromatographic methods have been applied to give “fingerprint” information on foulants. In size exclusion chromatography (SEC) or gel filtration/permeation chromatography, compounds are separated based on their size. It is usually applied to large molecules or macromolecular complexes such as proteins and industrial polymers. Different detectors like UV (Drews, 2010), RI (Ni et al., 2009) or organic carbon (Kuhn et al., 2007) are used. Chromatograms show more or less distinct peaks for biopolymers (including polysaccharides, some proteins and colloids), humic substances, building blocks, organic acids and amphiphilic or neutral low molecular weight compounds (Metzger et al., 2007).

In an attempt to identify specific proteins and thus to track down their origin, gel electrophoresis has recently been adapted to activated sludge samples (Kuhn et al., 2007). Similarly, excitation-emission matrix (EEM) fluorescence spectroscopy can yield a fingerprint of the present organics and thus gives information on the system's physiological state (Galinha et al., 2007; Kimura et al., 2009).

Fourier transform infrared (FTIR) spectroscopy has been applied to identify functional groups of organic molecules adsorbed on membrane surfaces (Nataraj et al., 2008; Loh et al., 2009). In addition to chemical analyses, several in situ imaging or visualization techniques have been applied recently. Le-Clech et al. (2007) compared scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM) and confocal laser scanning microscopy (CLSM) to characterize fouled membranes. SEM requires drying which might cause shrinkage of membrane pores and a collapse of fouling layers while ESEM can be applied to the wet sample. On the other hand, ESEM has a limited resolution (0.5 m in contrast to 0.01 m for SEM) and no cross-section can be obtained. The authors concluded that of the three techniques, only CLSM can differentiate between different types of foulants.

Depending on the used markers, it allows detection of polysaccharides (Yun et al., 2006) but also of proteins (Ferrando et al., 2005) and cells. It yields 3D images of the fouling layer which can be used to calculate its hydraulic characteristics like porosity. Multi-photon microscopy (MPM), too, yields 3D images in which cells and proteins can be differentiated and has an even higher penetration into the sample (Hughes et al., 2006). Zator et al. (2007) observed that fluorescent solutions of bovine serum albumin (BSA) and dextran showed less fouling than non-fluorescent solutions. This shows that CLSM which requires fluorescence needs to be applied with care.

Direct observation (DO) of fouling is also possible using a specifically mounted microscope. Initially introduced as direct observation through the membrane (DOTM) the set-up was modified to enable real-time visualization of fouling development on a hollow fibre membrane (Le-Clech et al., 2007). Its use, however, is limited to optically accessible systems such as dilute suspensions or single fibres.

So far, no in situ, non-destructive observation of fouling in MBR has been proposed. Real-time information on fouling can therefore only be obtained from actual filtration data.

2.2.4 Membrane fouling models

Sectional resistance model

In an MBR, coarse bubbles from aeration provide a cleaning mechanism for the immersed modules by scouring the membrane surface. Nevertheless, the shear force coming from aeration is unevenly distributed over the membrane surface, resulting in non-uniform fouling development over time. Li et al. (2008) applied a sectional approach to account for the uneven cake formation in determining total filtration resistance.

The membrane surface can be divided into equal fractional areas, $\Delta\varepsilon$, and separate total resistances R can be calculated, which consist of intrinsic membrane resistance R_m, pore fouling resistance R_p, and resistances due to dynamic and stable biofilms, R_{sf} and R_{sc}, respectively. The scheme of this model is showed in Figure 2-11.

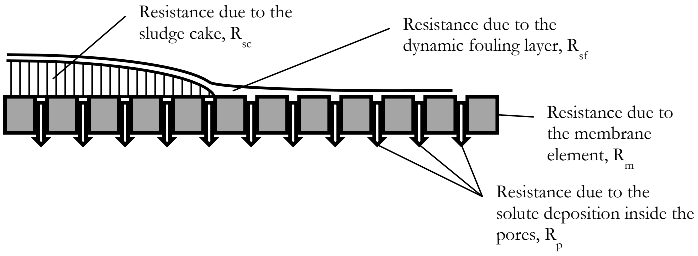

Figure 2-11 - Scheme of fouling development onto a membrane and resistances attributed to each layer

The total resistance is then evaluated in each section as:

$$R = R_m + R_p + R_{sf} + R_{sc}$$

The pore fouling resistance, R_p, is proportional to the amount of permeate produced and is given by:

$$Rp = r_p \sum J\theta_f$$

where r_p is the specific pore fouling resistance, J is the permeate flux, and θ_f is the filtration period of an operational cycle. R_{sf} is an expression of the specific resistance of the biomass in the dynamic film, r_{sf}, and the mass of the same film, M_{sf} (i.e., $R_{sf} = r_{sf}M_{sf}$). Similarly, R_{sc}, is equal to the product of the specific resistance of the sludge cake layer, r_{sc}, and the mass of biomass accumulated on the membrane surface, M_{sc} (i.e., $R_{sc} = r_{sc}M_{sc}$).

The mass of the sludge in the dynamic film can be determined from the following equation during the filtration period:

$$\frac{dM_{sf}}{dt} = \frac{24CJ^2}{24J + C_d d_p G} - \frac{\beta(1-\alpha)GM_{sf}^2}{\gamma V_f t + Ms_f}$$

The first and second term of the equation represent the rate of attachment and detachment, respectively, of solid matter onto the membrane surface. The attachment rate can be derived by considering the opposing forces acting on a particle as it approaches the membrane (Prieske et al., 2010). The attachment force divided by the sum of the two opposing forces gives the probability of the deposition of a particle on the membrane surface. The multiplication of this probability by the mass flux returns the rate of attachment (Chiemchaisri et al., 1993).

In the above-mentioned equation, C is the sludge concentration, J is the local permeate flux in the membrane section, C_d is the coefficient of the lifting force of a particle of diameter d_p, and G is the shear force on the section of the surface. The detachment rate can be assumed to follow a first-order kinetic process, i.e., $(dM_{sf}/dt)d = -K_dM_{sf}$. The rate coefficient, K_d, is thought to vary with the mass of the sludge film. It increases with M_{sf} and reaches a maximum with large values of M_{sf} so that a Monod-type equation, $K_d = \varkappa_r M_{sf}/(\varkappa_s + M_{sf})$, has been suggested (Li et al., 2008). In the detachment rate term, β is the erosion rate coefficient of the dynamic sludge, α is the stickiness of biomass particles, γ is the compression coefficient for dynamic sludge, t is the filtration time, and V_f is water production within the filtration period of the operation cycle. During the cleaning phase (no attachment occurs) the rate of detachment is described as:

$$\frac{dM_{sf}}{dt} = -\frac{\beta(1-\alpha)GM_{sf}^2}{0.1\gamma V_f \theta_f + M_{sf}}$$

The factor 0.1 in the denominator is because the compression coefficient during the cleaning period is reduced by a tenth of its original value. The fraction of sludge left after cleaning, ΔM_{sc}, adds to the stable sludge cake layer.

The sectional resistance model has been developed using a partially analytical approach. The model is intended to characterize membrane fouling in MBRs where the membranes are partially cleaned thanks to shear flow from aeration (Lubbecke et al., 1995). By dividing the membrane into sections and considering the resistance in each section, the model accounts for uneven cake formation due to varying shear distribution along the membrane surface. This transient model can therefore account for cleaning cycles and characterize fouling development over time (McGahey and Olivieri, 1993).

In another work (Bessiere et al., 2005), Authors studied the effect of stirring intensity on membrane fouling in a cross-flow microfiltration system and observed that finer particles (<50 μm) caused severe membrane fouling. However, Lee et al. (2006) found that in iMBR operation, the filtration performance enhanced with increase in airflow rate, despite a decrease in microbial floc size. Since activated sludge is a complex matrix being combination of particulates, colloids, EPS and SMP, it is difficult to correlate fouling rates/specific cake resistances with bio-particle sizes (Okamura et al., 2009). Therefore, further insight is necessary to understand factors affecting cake resistance (R_c) to precisely model membrane fouling behavior in a MBR system (Wang et al., 2001; Wang et al., 2005).

Fractal permeation model

A permeation model (based on Darcy's law) has been proposed (Meng et al., 2009) to analyze the permeability of the cake formed during the filtration process in MBRs. The microstructure of a cake layer is usually rather complex; therefore, the cake layer cannot be described by traditional geometry. Fractal theory can be applied in this context to characterize this irregular element in terms of its average properties. The authors first introduced a model to determine the pore area fractal dimension, D_s, of a cake layer:

$$B(\geq a) = S_c - A = C_0 (a)^{2-D_s}$$

where a is a threshold value for pore area, B is the total cake layer area (S_c) minus the sum (A) of all pore areas equal to or larger than a (i.e., A = Σa), and C_0 is a constant.

This model has been developed according to a previous fractal model (Ng and Kim, 2008; Huyskens et al., 2008), which had been proposed two decades years ago. The authors provided a procedure for physically determining the fractal dimension of a cake layer, which involves the use of an image analyzer to evaluate each pore area (Broeckmann et al., 2006). The equation can be applied to calculate the values of B from several defined threshold values of a. The fractal dimension can then be computed from the slope of the straight line through the plot of ln B vs. ln a. The permeability model provided by the authors has been derived by modifying the Hagen–Poiseulle equation for a flow passing through a tortuous capillary or pore:

$$q(a) = \frac{G}{g} \frac{\Delta P}{L(a)} \frac{a^2}{\mu}$$

where G is the geometry factor for fluid flow through a pore (i.e., π/128 for circular pores), g is the shape factor, a is equal to $g\lambda^2$, (λ being the average pore diameter) ΔP is the pressure gradient, L(a) is the length of a pore, and μ is the dynamic viscosity. Straight pores can then be assumed in the cake layer instead of tortuous ones, allowing the replacement of L(a) by a constant, L_0. In Figure 2-12 an illustration of the filtration process is provided.

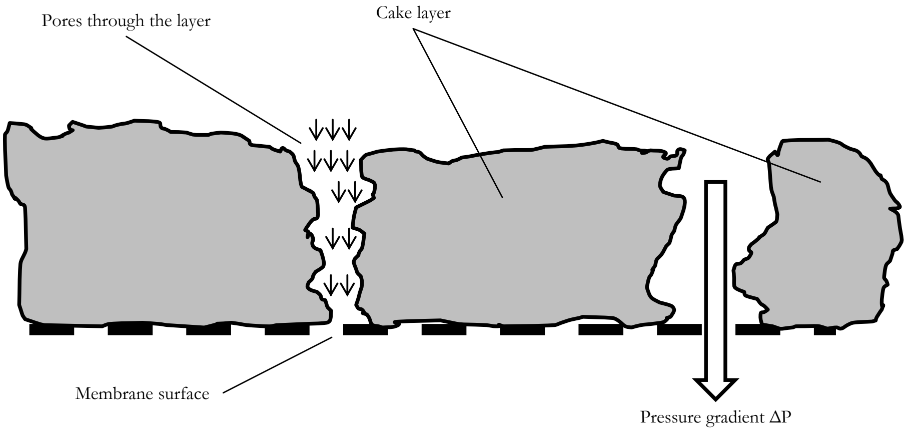

Figure 2-12 - Analysis of the effect of a cake layer on the water flow distribution

The specific flow rate can be obtained by dividing q(a) by a, and the infinitesimal flow rate dQ through an area dA is therefore expressed as:

$$dQ = -\frac{q(a)}{a} dA = -\frac{G}{g^2} \frac{\Delta P}{L_0} \frac{a}{\mu} dA$$

The portion of cake area, dA, is then:

$$dA = -C_0 \cdot (2 - D_s) \cdot a^{1-D_s} da$$

From which it can be derived the flow rate, Q:

$$Q = \frac{G}{g^2} \frac{\Delta P}{L_0} \frac{1}{\mu} C_0 \frac{2 - D_s}{3 - D_s} a_{\max}^{3-D_s}$$

The expression for the flow rate, Q, can be substituted into the Darcy's law to obtain the following equation for the permeability of a porous cake:

$$k = \frac{\mu L_0 Q}{\Delta P A_t} = \frac{G}{g^2} \frac{\Delta P}{L_0} \frac{1}{\mu} C_0 \frac{1}{A_t} \frac{2 - D_s}{3 - D_s} a_{\max}^{3-D_s}$$

The fractal permeation model is a method for determining the permeability of a cake on a membrane surface. The model involves only a few parameters that are easy to determine and does not require intensive computation (Hermia, 1982). However, the model has been only indirectly validated; therefore, more adequate verification is necessary to determine the model's reliability. Moreover, the model does not show how operational parameters and conditions affect cake resistance. Therefore, various parameters will have to be correlated with the pore area fractal dimension to determine their effects on cake resistance.

2.3 CONVENTIONAL WAYS TO CONTROL MEMBRANE FOULING

While an increasing number of studies is focusing on potentially innovative strategies to control the fouling phenomenon, at present full-scale MBR plants deal with fouling operating on (a) feed pretreatment, (b) flux, (c) aeration and (d) cleaning protocols.

2.3.1 Feed pretreatment

While CAS treatments do not require any particular kind of screens, MBRs should be protected with fine screens and sieves; deposits of hairs – whose daily loss can be estimated around 140-250 µg per person (Judd, 2010) – and other debris accumulate at the membrane interface, generating clogging and fouling. In particular, while HF membranes tend to accumulate hairs between the fibres, FS membranes show fouling when dewatering occurs over certain areas. If aeration fails to remove this solids built-up, sludge may accumulate, increasing the dewatered membrane area. In addition, entwined hairs may change the flow pattern and/or reduce the air scouring effect.

Mechanical pre-treatment of wastewater is therefore essential and crucial for the MBR process. There is still discussion ongoing on how to design the optimal pre-treatment system. This is mainly due to the fact that still today there is relatively poor knowledge about the ability of different pre-treatment units – mainly sieves – and entire pre-treatment systems to modify the raw wastewater in a way that avoids excessive deposit of solids at the membrane surface. A study published in 2008 (Kimura et al., 2008) showed that common 3-6 mm screens should be followed by fine (0.5-1 mm) screens, regardless of the membrane configuration.

2.3.2 Flux reduction

Concerning operating flux, a distinction has to be made: FS membranes usually operate at a steady flux, below the maximum sustainable condition; this means that no remedial measures are required apart from chemical cleanings. On the other hand, HF membranes commonly operate with an average flux that is higher than the sustainable one, therefore implementing several additional cleaning strategies, such as relaxation and backwashing, in order to allow the unit to cope with more frequent fouling.

Common practice showed that net fluxes of 18-25 LMH favor operation for iMBRs (Judd, 2010), even though MBR suppliers usually allow their products to be operated at fluxes much higher than normal values, in order to treat peak flows.

2.3.3 Aeration

In conventional aerobic biological wastewater treatment processes, oxygen is usually supplied as atmospheric air, via either immersed air-bubble diffusers or surface aeration. Diffused air bubbles (via fine-bubble aeration) are added to the bulk liquid (as in a CAS process, biological aerated filters (BAFs), fluidised bioreactors, etc.), or oxygen transfer occurs from the surrounding air to the bulk liquid via a liquid/air interface (Fang et al., 2006).

The oxygen requirement to maintain a community of micro-organisms and degrade BOD and ammonia and nitrite to nitrate can be found by a mass balance on the system (Beun et al., 2001; Bessiere et al., 2005; Metcalf and Eddy, 2003):

$$m_O = Q(S - S_e) - 1.42P_x + 4.33Q(NO_X) - 2.83Q(NO_X)$$

where m_O is the total oxygen required (g/day). The first term refers to substrate oxidation, the second refers to biomass respiration, the third refers to nitrification and the final term refers to denitrification. Certain terms thus disappear from the expression depending on whether or not the system is nitrifying and/or denitrifying.

Empirical correlation between flux and aeration have been proposed in a number of studies (Ueda et al., 1997; Monclus et al., 2011), and it has been shown that even if increasing aeration leads to improved critical flux values, allowing the MBR to work at higher fluxes, there is a threshold value beyond which further increases in aeration do not produce significant impacts on the membrane permeability. On the other hand, increasing aeration intensity is too much expensive, therefore in order to develop a sustainable procedure a balance has to be found between enhanced scouring effects and aeration costs.

The use of uniformly distributed fine air bubbles from 0.5 mm ports at a specific aeration rate of 0.5 $Nm^3/(m^2\ h)$ has been shown to provide both lower resistance and greater uplift compared to a coarse (2 mm ports) aerator (Sofia et al., 2004).

Mass transfer of oxygen into the liquid from air bubbles is defined by the overall liquid mass transfer coefficient ($k_L m/s$) and the specific surface area for mass transfer (a m^2/m^3). Because of the difficulties associated with measuring k_L and a, the two are usually combined to give the volumetric mass transfer coefficient k_La (per unit time).

The standard method accepted for determining k_La in clean water is detailed in ASCE, 1992. The rate of oxygen transfer into a liquid can be determined by:

$$OTR_{cleanwater} = ak_L(C^* - C)$$

where C and C^* are the dissolved and saturated oxygen concentration values in kg/m^3. For pure water and equilibrium conditions, C is found using Henry's Law. This can be converted to process conditions by the application of three correction factors (α, β and φ) which account for those sludge properties which impact on oxygen transfer:

$$OTR_{process} = \frac{OTR_{cleanwater}}{\alpha\beta\varphi}$$

Aeration also provides agitation to ensure high mass transfer rates and complete mixing in the tank. There is thus a compromise between mixing, which demands larger bubbles, and oxygen dissolution, which demands small, indeed microscopic, bubbles (Drews, 2010). Consequently, oxygen utilization, the amount of oxygen in the supplied air, which is used by the biomass, can be as low as 10%, and decreases with increasing biomass concentration. This can be quantified by the standard aeration efficiency (kg O_2/kWh):

$$SAE = \frac{OTRxV}{W}$$

where W is the power demand. The OTR into the mixed liquor can be increased by using oxygen-enriched air, but this increases costs and is rarely used other than for high-strength effluents when the oxygen limitation is reached. In an iMBR, additional aeration is also required for scouring of the membrane (Canales, 1994).

Changes in airflow have been shown to produce the largest changes in mass transfer in a coarse bubble aeration system (Judd, 1010), with kLa increasing with gas velocity in an airlift reactor.

Lim and Bai (2003) proposed that both the liquid and gas velocities impact on mass transfer, confirmed by experiments based on a jet loop MBR by Nagaoka et al. (1996). However, the authors of this paper also noted a linear relationship between the mass transfer coefficient and the liquid recirculation velocity. Also, increasing horizontal velocity has been shown to increase the value of k_La in an oxygen ditch in both pilot and full-scale plants (Judd, 2010).

2.3.4 Cleaning protocols

During MBR operation, when the TMP reaches values higher than 1 bar cleaning procedures take place in order to reduce both fouling and TMP.

In general, two separate approaches are available, the first being related to physical cleaning and the second depending on the use of chemicals.

Physical cleaning of membranes is achieved through backwashing or relaxation. Backwashing consists in providing an additional backwash flux of permeate after having stopped the operational flux. In this way, the membrane switches from an out-in to a in-out flux: this will clean fouled areas of the membrane, reducing the TMP. Drews (2010) found that backwash frequency had more effect on fouling removal than aeration intensity or backwash duration, even though there is no accordance on focal parameters of the process. Therefore, control systems have been developed in order to automatically optimize backwash duration and frequency depending on the monitored TMP value. In order to improve the fouling reduction rate, air backwashing has been proposed (Sombatsompop et al., 2006), recording an increase in the operational flux with a 15 minutes operation – 15 minutes backwashing scheme. Despite this result, air backwashing can lead to membrane drying out and then to problems of membrane integrity.

Membrane relaxation can lead to a diffusive back transport of foulants away from the membrane surface under a concentration gradient, which is also improved by the air scouring effect (Zhang et al., 2006). Membrane relaxation also allows filtration to be kept for longer periods before the need for chemical cleaning arises (Ng and Hermanowicz, 2005). Several studies (Zhang et al., 2006) demonstrated that relaxation can be successfully combined with backwashing for optimal results. Nevertheless, membrane relaxation seems to be particularly diffused among iMBRs.

To remove membrane fouling that cannot be removed by physical cleaning, chemical cleaning takes place, in the form of routine or intensive cleaning depending on the status of the membrane (Drews, 2010). Maintenance cleaning aims to reduce the frequency of intensive cleanings, and it can be performed with the module both in situ and off site. Intensive cleaning is required when operation is no longer possible because of the reduced permeability. Chemical cleanings are performed dosing sodium hypochlorite combined with citric or oxalic acid: the first aims to remove organic foulants, the second inorganic scalants.

Since the cleaning protocol depends on several factors, e.g. feedwater characteristics, chemicals used, aeration on/off cycle etc., the designed protocol cannot reach an optimum without taking into consideration a feedback control system.

2.4 CAUSES OF OCCURRENCE OF FOULANTS IN MBRS

Even if we suppose that the supernatant compounds reach the membrane surface, we cannot assume all conditions and cases to be equal. In other words, to evaluate the role of SMP on fouling, the influence of various parameters on the two key aspects – occurrence and concentration of SMP on the one hand and their properties like rejection, molecular weight and fouling potential on the other – must be taken into account (Fane, 2009).

Regarding the influence of MBR operating conditions on SMP occurrence and fouling potential, a number of hints have been gained over the years. Rosenberger and Kraume (2002) observed that the specific SMP concentration increased with sludge loading rate (F/M ratio) and decreased with sludge age. Grelier et al. (2006) found that the contribution of colloids to fouling decreased with increasing SRT. While overall SMP formation did not seem to have been significantly affected by unsteady operation, the nature or structure and hence the fouling propensity of the polysaccharides seemed to vary. It was shown that SMP formed primarily under severe substrate limitation have a higher fouling potential (Nagaoka et al., 2001). Toxic compounds and hydrodynamics or shear stress have also been identified to affect EPS and SMP concentration. Among the literature observations, the usual contradictions can also be spotted. To give just one example, more polysaccharides were found at high dissolved oxygen concentration by Yun et al. (2006), while typically low levels of oxygen give rise to higher SMP concentrations.

Reasons for such contradictory findings could again be multiple, complex and interacting influences which cannot be assessed independent of each other in full-scale trials, and often are even difficult to separate in the lab. In addition, influent SMP concentrations and the effect of partial SMP retention by the membrane are surprisingly often overlooked (Wozniak, 2009; Drews, 2010). Despite its name, what is measured as SMP does not necessarily have to be of microbial origin so even synthetic feeds can contain significant amounts, which will also vary over time (Judd, 2010). Real feeds obviously contain very different amounts and types of SMP depending on the origin of the wastewater and the residence time in the sewers.

This neglect of influent values and membrane retention on SMP accumulation in the tank might have led to the general perception of SMP production or release whenever an increase in SMP concentrations was observed. A simple mass balance, however, reveals a net SMP elimination of typically about 80%, and that only under extremely adverse conditions a net release can be observed (Drews, 2010). Wang et al. (2009) found a wider molecular weight spectrum of SMP in the biomass than in the feed. Hence, it is appropriate to speak about net elimination because apparently the disappearance of SMP by adsorption, biodegradation etc. can be accompanied by the release of a smaller amount of different products and thus can cause a shift in the molecular weight spectrum. This, on the other hand, can also be brought about by partial retention. Typically, carbohydrates are rejected to a greater extent than proteins and thus accumulate in the mixed liquor (Pan et al., 2009; Meng et al., 2009). This accumulation can be enhanced by the proteins' higher biosorption and biodegradation rate (Drews, 2010). In a 10-month study on the fate of carbohydrates, proteins and humic substances in a pilot-scale MBR it was confirmed that $DO_{M}in$ the feed were mainly composed of readily biodegradable matter while bound EPS were mainly composed of slowly biodegradable matter. LC-OCD analysis, together with results obtained from accompanying batch tests, suggested that bound EPS are the most important source of $DO_{M}in$ the sludge suspension (Meng et al., 2009). Gel permeation chromatography showed that the biomass supernatant contained more high and less low molecular weight constituents than the feed (Charlery et al., 2009). All samples contained glucose derived compounds with a degree of polymerization equal to three, with more of these 3-glucose-units compounds present in the feed and similar amounts in the sludge and permeate (Charlery et al., 2009). Ion exchange chromatography of hydrolyzed samples revealed that in contrast to the sludge and feed, very little glucose and fructose derived oligo- and polysaccharides were present in the permeate. Thin layer chromatography of the hydrolyzed membrane extract confirmed that glucose derived oligo- or PS were retained, as well as xylose and to a lesser extent arabinose, rhamnose and fructose derived compounds (Sun et al., 2008; Charlery et al., 2009; Chae et al., 2009). Arabi and Nakhla (2008) investigated the impact of feed protein/carbohydrate ratio on biomass properties and fouling. As the ratio was increased, the amount of SMP including the carbohydrate fraction rose, although the ratio was increased by a reduction of the carbohydrates concentration. At the same time, EPS concentration was lower which in turn decreased floc sizes and thereby increased cake resistance. Other properties were also found to change. Hydrophobicity of the proteins in the EPS increased while that of the carbohydrates decreased, and their molecular weight distributions shifted. From their partially diametrically opposed findings, the authors concluded that SMP composition depends on, but is not directly correlated to, the feed composition (Pollet et al., 2009).

Besides feed characteristics and retention capacity, a number of operating and ambient conditions impact on SMP occurrence and properties.

SRT

Based on the concept of utilization and biomass associated products (Lu et al., 2001), SRT has been identified as the main parameter influencing SMP concentration (Jiang et al., 2008) with SMP or loosely bound EPS concentration typically dropping at higher SRT. In terms of fouling propensity, less fouling was repeatedly observed to occur at higher sludge ages (Trussell et al., 2009). SRT also seems to be an important factor for the particular relevance of other factors like temperature (Judd, 2010) or PS for fouling. Even the linear correlation published by Rosenberger et al. (2006) was only observed for an SRT = 8 d and not for an SRT = 15 d. In a study where the influences of MLSS, HRT and SRT were investigated separately, Grelier et al. (2006) observed that both fouling rate and the colloids' contribution to the total resistance as determined after sample fractionation decreased with higher SRT. Trussell et al. (2006), who reported fouling rates as the drop in permeability over 10–14 d of stable operation, confirm this trend for fouling rates. However, they found that the contribution of SMP to the total filtration resistance increased with increasing SRT from 2 to 10 d (Trussell et al., 2009) which might not only be caused by the difference in SRT. Ahmed et al. (2007) showed that the specific cake resistance decreased with SRT. In a sequencing batch MBR, similar molecular weight distributions (determined by membrane fractionation) were found at different SRT, but SMP rejection decreased with increasing SRT (Jiang et al., 2003). This was explained by the different actions of the cake/biofilm and possibly by a change in hydrophobicity, since SUVA in the effluent also increased with SRT. Al-Halbouni et al. (2008) could confirm the decreasing relevance of polymers at higher SRT by analyzing the amount of polymers attached to membranes that had been in operation in two parallel pilot MBRs. At SRT = 40 d, 40 times less proteins and 5 times less PS were present on the membrane than at 23 d. The monosaccharides found on the membrane were different from those in the supernatant. Independent of SRT, mainly glucose and rhamnose were found on the membrane while SMP composition varied with SRT. EEM fluorescence spectroscopy showed that proteins were more important at lower than at high SRT.

Temperature

Temperature affects permeate viscosity, which is commonly corrected in order to compare permeabilities or resistances obtained at different temperatures. However, temperature also affects filtration in other ways. Sludge viscosity and in turn shear stress/forces close to the membrane surface, deflocculation, release of EPS, diffusitivity, biodegradation, and adsorption all depend on temperature. That temperature has different effects on permeability was recently confirmed at full scale over 2 years (Lyko et al., 2008). As temperature was increased, CST decreased, while at the same time, filterability (measured in terms of a filtration index in lab scale) was not clearly correlated. Carbohydrates concentration showed a slight negative correlation with temperature, however, the height of the macromolecular peak correlated only with CST but not with the filtration index (Wisniewski and Grasmick, 1998). Apparently, the properties of the carbohydrates had changed over time.

Miyoshi et al. (2009) investigated the influence of seasonal variations on reversible and irreversible fouling. Two separate MBRs with different SRTs were operated in parallel for about 200 d including high and low temperature periods. Seasonal variations of both reversible and irreversible fouling were observed for the MBR with short SRT (13 d). Reversible fouling was more significant in the low temperature period, while irreversible fouling developed more rapidly in the high temperature period. Only the rates of reversible fouling could be related to the concentration of dissolved organic matter, the characteristics of which differed depending on the temperature period. In contrast, in the MBR with long SRT (50 d), there were no significant seasonal variations in either type of membrane fouling.

Due to the fact that temperature influences metabolic rates like any other reaction kinetics, it again cannot be discussed on its own.

Oxygen sources

For mineralization of SMP, oxygen is required. Apart from being a reaction partner, dissolved oxygen (DO) is also necessary to keep the activated sludge aerobic. Low levels of DO lower the cell hydrophobicity and thus cause floc deterioration (Drews, 2010). Hence, deflocculation, increased SMP concentrations and a deterioration in filterability can be the result of oxygen stress. However, such results of even prolonged anoxic conditions of up to 3 d can be undone within only a few hours of aeration (Geilvoet et al., 2008). As already mentioned, influent SMP are normally eliminated to a large extent during biological treatment. In a pilot MBR fed with domestic wastewater and operated with irregular sludge withdrawal, net elimination was around 80% as long as DO concentration was above 1 mg/L (Al Malack, 2006; Judd, 2010). From modeling SMP production and uptake, Lu et al. (2001) also concluded that a dissolved oxygen concentration below 1 mg/L leads to elevated SMP concentrations. Additionally, nitrate can be used for oxidation. Lu et al. (2001) proposed a non-competitive inhibition mechanism for SMP uptake with oxygen inhibiting the use of nitrate for oxidation, and a linear dependency on biomass concentration for release. DO also influences EPS and SMP properties. In a study on the distribution of EPS in aerobic granules, Wang et al. (2005) found that the granules' aerobic outer shell contained poorly soluble and rather hydrophobic EPS, whereas the anoxic inner core was filled with readily soluble and biodegradable EPS. Yun et al. (2006) and Yoon et al. (2006) conducted studies on biofilm structure in aerobic/anoxic (when DO <0.1 mg/L) MBRs and investigated the porosity and EPS surface coverage by CLSM. The rate of fouling was 5 times higher in the low DO MBR. The authors reported that not only the amount of EPS but also its spatial distribution inside the biofilm might affect membrane filterability. They found that the amount of polysaccharides extracted from the aerobic biofilm was greater than that from the anoxic biofilm despite the smaller resistance of the aerobic film. The ratio of proteins to polysaccharides was also higher in the high DO MBR and the microbial communities differed significantly. The confocal images of anoxic biofilms showed that they were highly spread out and that the distribution of polysaccharides was more uniform than in the aerobic biofilm where the porosity of the PS structure was high. Min et al. (2008) investigated the influence of DO concentration on the molecular weight of the prevalent polymers. The already predominantly macromolecular fraction (about 60% of protein were larger than 100 kD at 3.7 mg DO/L) was even larger at 0.2 mg O/L (80%), while the overall protein concentration was the same. No clear correlation was found between filtration resistance and EPS or DO concentration. Since the feed was not analyzed, and in addition to the DO concentration SRT was changed (from 77 to 30 d) in order to obtain the same MLSS, however, conclusions are questionable.

Nitrification/denitrification activity

In a mixed population, the different species will contribute differently to the foulant properties. To study the effect of nitrifier activity, DO concentration and temperature were changed in a step-wise manner in lab-scale trials, and allylthiourea (ATU) was added to the mixed liquor to inhibit ammonia oxidation and thus to prevent nitrate build-up (Drews, 2010).

Temperature was found to impact on SMP retention and on temperature corrected fouling rate; both were higher at low temperatures. DO concentration showed no unambiguous influence on rejection. As can be seen, lowering temperature caused an immediate rise in supernatant SMP concentration accompanied by an increase in rejection (Geissler et al., 2005). Apparently, large molecules were produced or – maybe more likely, considering the effect of temperature on reaction rates – less large molecules entering the plant were eliminated. This effect was reversible when temperature was increased again. Inhibiting nitrifiers, too, immediately increased rejection. While temperature caused a rejection change mainly through a change in sludge supernatant concentration, the addition of ATU changed both sludge and permeate concentrations (Drews, 2010). Since rejection was almost unaffected by temperature in the presence of ATU, it was concluded that temperature only has an indirect effect on rejection by decreasing nitrification rates at low temperatures. In repeated runs with ATU addition, an increase in PS and SMP rejection was observed. A slight correlation between ammonia oxidation rate and protein rejection was typically observed (Judd, 2010). In three lab trials, however, no dependence of protein rejection on ammonia oxidation rates was found. In these runs, in contrast to the others, significant amounts of nitrite were detected, i.e., apparently nitrite oxidation was somehow inhibited. A roughly linear correlation between protein rejection and nitrite concentration was observed in these three trials. Here, the rejection increase was mainly due to a decrease in permeate concentration.

Elevated rejection and very high concentrations of PS up to 150 mg/L were found in a pilot plant during a period of low nitrification activity. However, at the same time, fouling was rather low (Brepols et al., 2008). This could indicate that under these conditions SMP were mainly too large to cause internal fouling but rather formed a loose cake. The inhibition of nitrite oxidizers therefore seems to be relevant for the lack of SMP that are small enough to enter and block the pores and to pass through the membrane.

The typical influence of pH on protein retention, which increases with pH, was found not to follow the same trend (in fact it was completely opposite) in the presence of nitrite, which supports the hypothesis that nitrite oxidizers play a significant role in determining the properties of SMP. Larsen et al. (2008) observed that typical representatives of ammonia and nitrite oxidizers formed strong microcolonies, with Nitrospira spp. being even stronger than Nitrosomonas oligotropha colonies. Even under high shear, only the largest N. oligotropha colonies fragmented, and deflocculated fractions of both species were much lower than those of biomass in general. The authors hypothesized that the reason for these higher adhesion forces could be a stronger entanglement of the species' EPS, but quite possibly their properties are also different. Trussell et al. (2009) compared a non-nitrifying (SRT=2d) MBR with one operated at 10 d. They found that the fouling rate was higher in the non-nitrifying MBR but the resistance against clean water flux which was measured in each case when 70 L/(m^2 h bar) were reached was lower. Fewer proteins and more carbohydrates were found in the 10 d MBR but the carbohydrates' molecular weight was much lower and only 3% were rejected. In the 2 d MBR, similar concentrations and molecular weight distributions were found in the feed and supernatant and a lot more SMP were rejected. By fractionation, Geilvoet et al. (2006) showed that proteins and PS present in denitrification, nitrification and membrane tanks, can have substantially different sizes. In the full size MBR at Monheim (Drews, 2010), high fouling occurred during periods of high nitrate concentrations. Over 3 years, temperature corrected permeability followed the nitrate profile closer than it followed the temperature profile (Kraume et al., 2009).While it is yet unclear if there is a correlation between permeability and nitrate concentration or if this only accidentally happened in parallel, it gives another indication of the potential importance of N-components even at full scale. More investigations, however, are necessary to support this hypothesis, especially because it is in contrast to findings by Thanh et al. (2010) who investigated sludge and effluent characteristics of a sequencing batch airlift reactor (SBAR) with aerobic granular sludge bioreactor coupled with membrane filtration. In their study, the presence of nitrate and aerobic/anoxic conditions improved the sludge characteristics in terms of biomass retention, settling ability and fouling potential (Gao et al., 2004). The soluble fraction of the SBAR effluent contained mainly hydrophilic substances when nitrate was present in the wastewater. Kim and Nakhla (2010) subjected adapted nutrient removal sludge and CAS sludge to denitrifying conditions and compared the resulting filtration characteristics. Under denitrifying conditions, the adapted sludge showed less pore blocking. MFI, SMP concentration and carbohydrate/protein ratio were smaller, and the hydrophobicity of the bound EPS increased. In the CAS sludge, both MFI and SMP concentration increased. Apparently, different populations react differently to their oxygen and N-compounds environment.

The rate of change

Sudden temperature changes have been observed before to yield spontaneous changes in SMP concentration. Yang and Li (2009) investigated the response of CAS sludge to different step changes (in SRT, loading rate or carbon source) and observed that the amount of loosely bound EPS immediately increased when SRT was changed, and settleability (SVI) worsened. All changes yielded a sudden increase of effluent suspended solids, so deflocculation seems to have occurred.

No correlations were observed between tightly or loosely bound EPS and specific filtration, flocculation and settleability. Such property changes were reversible as the biomass became accustomed to the new situation after a couple of days, although the biomass used in their study was fed only once a day even under so-called steady state conditions. The rate of change therefore might be even more important than the new condition itself, because it imposes a shock on the biomass that takes a while to get accustomed to by floc restructuring, metabolic or population changes, etc. Especially the latter is a process with relatively high time constants.

By changing the ratio of monovalent over polyvalent cations in the influent, deflocculation–reflocculation events were induced by Van den Broeck et al. (2010). A high ratio resulted in severe sludge deflocculation and worsened filtration characteristics. A low ratio influent was subsequently fed, and within 3 weeks, the sludge reflocculated and filtration characteristics improved significantly.

Parameter Interactions

As seen above, it is difficult to relate observed effects to a single cause. Especially in real plants but even in controlled lab-systems, too many interactions occur between the various operating, biological and ambient conditions, which cannot be changed independent of each other. Thus, it is also likely that fouling causes must be searched for in a combination of parameters or conditions, which individually might even show opposing effects (Ducom et al., 2002). In that context, statistical analysis can be a useful tool. By applying multivariable analysis to data from a 12 months monitoring campaign of 4 pilot to full-scale MBRs it was found that TEP concentration (bound and soluble), temperature and nitrate concentration correlated with 95% of the critical flux (in situ flux stepping with BFM) data (Drews, 2010).

Influences on fouling agents

Multiple and complex interactions occur between operating or ambient conditions and SMP elimination, rejection and fouling propensity. Therefore, what discussed here highlight the following:

- Influent concentration and retention by the membrane need to be taken into account in the interpretation of results.
- DO and nitrate concentrations appear to have an impact on SMP elimination and thereby on SMP concentration with SMP elimination being lower at low availability of oxygen sources.
- Especially protein rejection was found to be influenced by nitrification activity and thus by temperature (Song et al., 2008). Nitrite oxidizers seem to be responsible for the formation of smaller SMP compounds that can pass the membrane. The buildup of nitrite might thus be used as an indication of increased SMP rejection or lower permeate concentration.

- Sudden changes can yield spontaneous SMP release and increase in fouling rates as well as a deterioration of other biomass properties. Therefore, to avoid fouling in MBRs, special attention needs to be paid in small or decentralized plants where operating and environmental conditions are subject to higher fluctuations with steeper gradients than in large plants (Gujer et al., 1999).
- The answer in the quest for a fouling indicator might be found in a combination of several parameters.

In considering the above conclusions, it must be noted that their relevance for long-term operation of full-scale plants needs to be examined. Mechanisms might still be different or the extent of a particular contribution to fouling could be exceeded by another factor.

2.5 EXTRACELLULAR POLYMERIC SUBSTANCES IN MBRS

EPS, metabolic products of active bacterial secretion (Drews, 2010; Judd, 2010), can be found either in a soluble form (also termed as soluble microbial products e SMP) or bound to cells or flocs in the reactor forming the cohesive matrix of the biofilms. Bound EPS consist of proteins, polysaccharides, nucleic acids and lipids accumulating on the bacterial cell surface (Belfort et al., 1994). The EPS strongly affect the microbial microenvironment heterogeneity including changes in porosity, density, water content, sorption properties, charge, hydrophobicity, and mechanical stability (Flemming and Wingender, 2001). One of the most effective MBR operating parameters with an impact on fouling propensity is solids retention time (SRT) or sludge age. SRT affects various sludge properties such as floc size, bound and soluble EPS content, and settling characteristics (Le-Clech et al., 2006).

Contradictory reports regarding a relationship between SRT and membrane biofouling show that even though higher SRT leads inevitably to increase of MLSS concentration, this in itself may not necessary lead to greater fouling. In general, optimal SRT, reported in plethora of studies between 20 and 50 days, is required to achieve a minimal fouling tendency (Meng et al., 2009; Drews, 2010; Drews and Kraume, 2005).

Improved membrane permeability was observed at longer SRT of 10 and 20 days in comparison to SRT of 3 and 5 days. The results were attributed to elevated concentrations of SMP and EPS concentrations that were observed to induce membrane fouling rate when SRT was decreased (Ng et al., 2008). Cho et al. (2005a) showed that as SRT decreased, the amount of bound EPS in the sludge flocs increased (Cho and Fane, 2002; Brauns 2003, Brauns et al., 2005). Hanft (2006) has reported that membrane fouling rate increased with increasing SRT of 30, 50, 70, and 100 days due to a large amount of foulants and high sludge viscosity (Drews, 2010). In contrast, Lee et al. (2009) tested three labscale submerged MBRs at SRT of 20, 40, and 60 days with a constant permeate flux and no major change in EPS concentration was observed as SRT increased (Lee et al., 2009). In another study, at elevated MLSS concentrations from 7 to 18 g/l corresponding to an increase in SRT from 30 to 100 days, fouling rate was twice for the extended SRT (Chaize and Huyard, 1991; Chang and Kim, 2005). This increase was probably due to the raised viscosity at the high MLSS concentration that attenuates the effect of bubbling and scouring of the membrane surface. Not surprisingly, fouling rate increased nearly 10 times when SRT was lowered from 10 to 2 days, probably due to the increased levels of EPS production (Trussell et al., 2006).Chang and Lee (1998) found that when the SRT was increased from 3 to 8 and to 33 days, a significant increase in sustainable flux was observed (Chang and Lee, 1998). The reduced fouling rates associated with a decrease in sludge production rates at longer sludge ages, is usually attributed to lower EPS concentrations in the reactor (Ross et al., 1992; Sakai et al., 1997). In addition, increasing SRT could enhance the development of slow growing microorganisms that are able to consume polysaccharides and proteins as substrates and produce less biopolymers (Masse et al., 2006). Overall, it is likely that there is an optimal SRT, between the high fouling tendency at very low SRT and the high viscosity of mixed liquor at very long SRT. EPS play a major role in the cohesion of the sludge flocs in the MBR as well as the cohesion of the biofilm layers located on carriers in the HG-MBR systems. EPS are also in charge of biofilms viscoelastic properties which in turn, can strongly affect the microbial flocs and biofouling layer resistance to shear. Eventually, EPS are recognized as the most direct and significant factor affecting biofouling in MBRs (Laspidou and Rittmann, 2002; Le-Clech et al., 2006). Soluble EPS in the MLSS was reported as an important factor influencing membrane fouling. A high concentration of soluble EPS was shown to boost membrane fouling tendency (Kimura et al., 2008). Fabrega et al. (2009) showed that soluble EPS concentration increased at shorter SRT, in which total proteinconcentrations was higher than polysaccharides in the MLSS supernatant, whereas the total polysaccharide content was higher than the protein in the flocs attached to the membrane surface causing a significant fouling. By increasing the SRT, soluble EPS content was decreased on the membrane surface and membrane filtration resistance was reduced. EPS production and accumulation on the UF membranes in MBR systems is a complex process influenced by several factors like the substrate composition, mechanical stress, organic loading rate, MLSS concentration, presence of soluble EPS compounds and membrane properties (Essemiani et al., 2001; Kromkamp et al., 2006).

2.6 TRANSPARENT EXOPOLYMER PARTICLES IN MBRS

Transparent exopolymer particles (TEP) are gel-like sticky particles consisting mainly of acidic mucopolysaccharides, ubiquitous in natural waters and measuring up to 100 s of micrometers (Passow and Alldredge, 1995). They are predominantly formed out of algal exudates, bacterial mucus and particular material from the gelatinous envelopes surrounding phytoplankton. Hence, they are found abundantly in oceans as well as in freshwater, wastewater and groundwater (Berman and Parparova, 2010; Kennedy et al., 2009; Passow and Alldredge, 1995). For more detailed information about TEP, the reader is referred to the elaborate review by Passow (2002). These studies only comprised particular TEP (pTEP > 0.4 mm) but recently, colloidal TEP (cTEP) was described (Villacorte et al., 2009). This fraction is similar to pTEP but passes 0.4 mm membranes and is retained on 0.05 mm. In these studies, cTEP contributed for up to 90% of total TEP concentrations (Villacorte et al., 2009, 2010). Since the staining method was developed to visualize these hitherto overlooked particles (Alldredge et al., 1993), they have mostly drawn the attention of oceanographers in relation to organic carbon cycling (Passow, 2002). More recently, their importance in membrane technology was recognized. Berman and Holenberg (2005) introduced the concept that TEP can induce biofouling on surfaces. Once attached to a membrane, these particles serve both as attachment

site and nutritious substrate for microbial growth. Furthermore, the efficiency of RO pretreatment systems in preventing TEP from reaching the sensitive membranes was verified since up to 70% of all TEP in influent water sticks on reverse osmosis (RO) membranes (Villacorte et al., 2009). Several combinations of sand and membrane filtration were able to remove pTEP for 30 up to
100%. In contrast, cTEP, which is most abundant, was rarely removed for more than 50% (Bar-Zeev et al., 2009; Kennedy et al., 2009; Villacorte et al., 2010). Moreover, this fraction can easily transform to new pTEP and hereby block pores that would not be blocked by the smaller cTEP. Recently, the positive correlation between TEP concentrations and capillary suction time, a common fouling indicator, was shown in a full-scale MBR treating domestic wastewater (de la Torre et al., 2008). In a similar system, multivariate data analysis related 95% of the variation of critical flux values to TEP, nitrate and temperature (de la Torre et al., 2010). Besides, Berman et al. (2011) stated that early deposition of extracellular polymeric substances (EPS) on membranes only originated from TEP in the feed water instead of being excreted by active bacteria developing a biofilm. This indicated that TEP can be an important characteristic of the incoming water in relation to the initiation of biofilms (Bar-Zeev et al., 2009; Berman et al., 2011).

Meanwhile, many studies have reported the abundance of TEP in marine water, surface water, waste- and groundwater. In contrast, their occurrence in drinking water treatment systems has, to our knowledge, only been described once so far (Villacorte et al., 2009). In this study, the final RO treatment could remove the last part of the total TEP.

However, the limited TEP removal efficiencies in several RO pretreatment systems like combinations of sand filtration, coagulation and ultrafiltration (UF) suggest the possibility of TEP reaching the drinking water in systems where no RO is present in the end of the treatment line (de la Torre et al., 2010). Furthermore, the putative role of TEP in biofilm formation could thus have safety implications for the drinking water distribution network. Waterborne pathogens like Legionella species use biofilms both for growth and protection against biocides (Szewzyk et al., 2000; Williams and Braun-Howland, 2003). TEP occurrence in drinking water can provide us new insights about biofilm prevention strategies.

2.7 BIO-ENTRAPPED MEMBRANE REACTORS

In recent years, extracellular polymeric substances (EPS) and/or soluble microbial products (SMP) have been established as a main cause of membrane fouling (Cho et al., 2005; Jarusutthirak and Amy, 2006; Liang et al., 2007; Malamis and Andreadakis, 2009; Meng et al., 2009). Bound EPS are extracellular components tightly attached to the biological flocs, whereas soluble cellular components are soluble EPS or SMP from microbial growth and decay, as well as from dissolution of bound EPS (Ramesh et al., 2006; Ng et al., 2010). EPS and SMP typically consist of polysaccharides, proteins, lipids, and nucleic acids (Le-Clech et al., 2006; Liang et al., 2007). Found in most biologically treated effluents, SMP contributes significantly to soluble organic matter and Chemical Oxygen Demand (COD) of the effluent (Barker and Stuckey, 1999; Zhou et al., 2009). In addition, polysaccharide-like and protein-like substances are found predominant in EPS and/or SMP (Rosenberger et al., 2006; Le-Clech et al., 2003; Frølund et al., 1995; Malamis and Andreadakis, 2009), though the species of these substances have not been well defined.

Depending on its nature and molecular size, SMP may form a cake layer on the membrane surface or penetrate into the membrane pores (Jarusutthirak and Amy, 2006; Rosenberger et al., 2006; Meng et al., 2009). The behavior of SMP in membrane fouling is complex because of its disparate molecular weight (MW), hydrophobicity, and zeta potential (Barker and Stuckey, 1999; Jarusutthirak and Amy, 2006; Pan et al., 2010). SMP comprises a wide range of MW ranging from <1 kDa to 0.45 mm (Barker and Stuckey, 1999; Malamis and Andreadakis, 2009; Ni et al., 2010). Further research is warranted on how MW distribution and characteristics of SMP influence membrane fouling.

Studies were undertaken that investigated moving bed biofilm reactor (MBBR) coupled with membrane as an alternative to the conventional MBR (Artiga et al., 2005; Ivanonic et al., 2006; Lee et al., 2006; Leiknes and Ødegaard, 2007). Yang et al. (2009) found that moving bed membrane bioreactor (MBMBR) produced more biomass in the effluent leading to increased membrane fouling than did CMBR. SMP in MBMBR were found to be more abundant than in CMBR. The objective in these studies of MBBR was to reduce MLSS in MBR, as ours was in developing the BEMR. Reducing MLSS enables less frequent backwashing and reduces downtime to clean the membrane. Contrarily, high MLSS in MBRs may increase non-Newtonian viscosities that hamper oxygen transfer and require additional energy for pumping (Drews and Kraume, 2005).

A new BEMR has been developed in the present study, that reduced suspended biomass and increased SRT in the reactor with the objectives to achieve high organics removal in a more facile operation with a short start-up period. As membrane fouling may differ between the new BEMR and conventional MBR, we have investigated TMP and their characteristics in membrane fouling of both reactors at various HRTs, and further evaluated membrane cleaning of reactors for comparison. An overall study goal is to reduce membrane fouling commonly encountered in MBRs.

2.7.1 Advantages and disadvantages of MBRs for removing xenobiotics

As MBRs exhibit a better behavior in the removal of pharmaceuticals than CAS treatment, their implementation should be encouraged on a wide basis. This will benefit water treatment and the environment. Biosolids concentration is higher in MBRs than in CAS so biological activity and concentration of filters has to be high to serve the biomass. Physical separation removes non-biodegradable compounds and leaves only those to be removed by biological activity. Moreover, a reduced footprint is offered as the MBR, because its compact process design of 50 to 80% less space than conventional treatment plants saves space. Lower operational costs may be generated when compared to CAS treatment, which would be needed for larger tanks along with reduced need of labour, as automation is increased (Bèrubè et al., 2006). Furthermore, the fact that the biomass is separated from the effluent through the MBR reduces the need for a final effluent, leading to even more efficiency in terms of energy and space. The organic solids collected from the MBR can be converted to biosolids, which can be used to produce energy. They can be converted to methane in digesters or can be burned to produce other forms of energy. As a result, costs on energy and aeration are saved, in combination with ecological benefits. On the downside, high-pressure systems such as MBRs which needs hydraulic pressure exerted on the wastewater for filtration, the need for pre-treatment to prevent fouling which requires space, the handling and disposal of the final concentrate along with the removal and change of membranes every 3-5 years to avoid reduced recovery rates may add cost to balance the cost savings from energy and space saving.

3 MATERIALS AND METHODS

Research activity related to the doctoral program has been carried out at the University of Salerno – Civil Engineering Department, SEED, and at the University of Washington – Civil and Environmental Engineering Department. Research carried out in the first phase (Jan – Dec 2012) has been developed at the University of Salerno and focused on the control of the compressibility of fouling layers. Research carried out in the second phase (Jan – Aug 2013) has been developed at the University of Washington and focused on Bio-Entrapped Membrane Reactors (BEMR) and Trasparent Exopolymer Particles (TEP) determination. Research carried out in the third and final phase (Sep – Dec 2013) has been carried out at the University of Salerno and focused on MBRs and TEP/EPS determination.

3.1 MATERIALS

3.1.1 Wastewater samples

The wastewater used in this study was prepared according to different studies. For the first phase (fouling layer compression, P1), synthetic wastewater has been prepared, in which a 20 mg/L D-glucose equivalent concentration was added to simulate biological degradation (Judd, 2010). Synthetic wastewater composition for P1 is shown in Table 3-1.

Table 3-1 - Synthetic wastewater composition for P1

Compound	Concentration [mg/L]
NaCl	1168
$NaHCO_3$	0,084
Sodium alginate	64,1

The feed concentration for the polysaccharide was determined using the calibration curve at an absorbance λ_{480} (Perkin-Elmer, UV/VIS Lambda 12), in order to obtain a D-Glucose concentration of 20 mg/L.

The feed polysaccharide suspension (Figure 3-1) was prepared adding 20 mM NaCl (Carlo Erba, Italy), 1 mM $NaHCO_3$ (Nacalai Tesque, Japan) and 64,1 mg/L $NaC_6H_7O_6$ (Sigma-Aldrich, US).

Figure 3-1 - Synthetic feed for P1 at a D-glucose concentration of 20 mg/L

After entering the reactor through the inlet tube, the solutions passes over the membrane, and permeate exits the system. In order to determine the sodium alginate size distribution, samples have been collected in the membrane reactor and analyzed using a Mastersizer (Malvern Instruments, Mastersizer2000).

For the second and third phase, a synthetic influent has been prepared as a feed for the biological oxidation step (Yang et al., 2002). Synthetic wastewater composition for P2-P3 is shown in Table 3-2.

Table 3-2 - Synthetic wastewater composition for P2-P3

Compound	Concentration [mg/L]
$C_{12}H_{22}O_{11}$	267.85
$(NH_4)_2SO_4$	133.93
KH_2PO_4	141.16
K_2HPO_4	286.62
$MgSO_4{\cdot}7H_2O$	21
$MnSO_4{\cdot}H_2O$	2.68
$CaCl_2$	3.8
$FeCl_3{\cdot}6H_2O$	0.14

The synthetic influent was prepared daily and continuously stirred in order to prevent settling and allow uniform distribution of added compounds. Throughout the study, the wastewater had a pH of 6.6 ± 0.1.

3.1.2 Experimental setups and membranes

For P1, a laboratory scale aerobic membrane reactor, consisting of a 5 L storage tank followed by a 2 L cylindrical reactor, was used for the treatment of the synthetic solution described above. The tank was equipped with a stirrer rotating at 500 RPM (VELP, AREX). The membrane module shown in is the ZW-1 (Zenon GE, US), pore size 0.04 μm and surface area 0.047 m^2 to retain solids in the reactor.

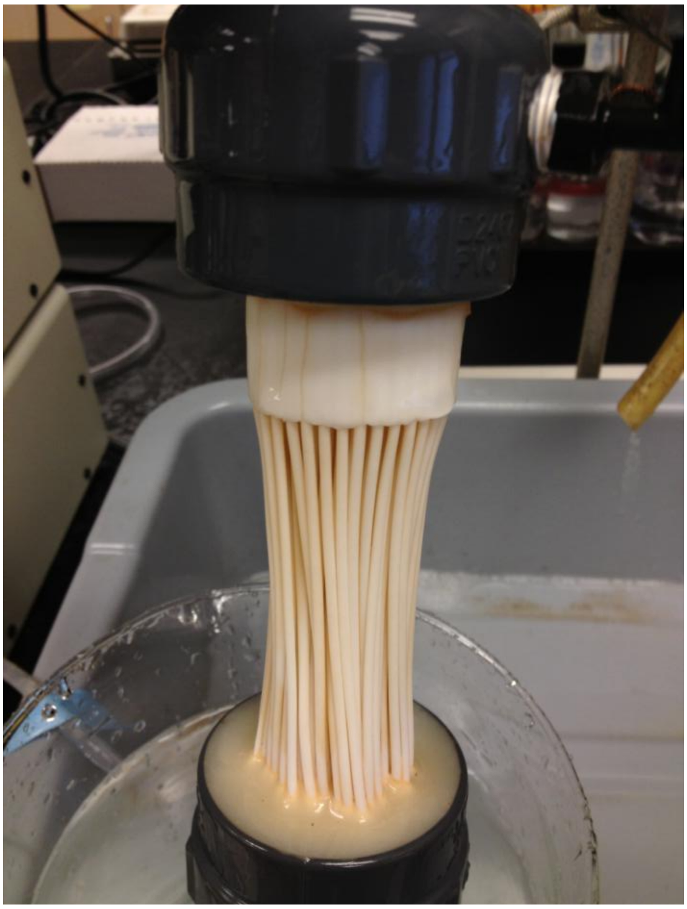

Figure 3-2 – ZeeWeed-1 UF membrane module (GE Zenon, US)

The membrane has been produced in PVDF (Polyvinylidene fluoride). Its characteristics are shown in Table 3-3.

Table 3-3 - ZW-1 Membrane properties

Parameter	Value
Membrane material	Polyvinylidene fluoride (PVDF)
Module type	Hollow fiber
Membrane pore size (mm)	0.036
Membrane surface area (m2)	0.046
Outer/inner diameter (mm)	1.9/0.8
Maximum operating temperature (°C)	40
Operating pH range	5.0 - 9.5
Cleaning pH range	2.0 - 10.5
Maximum operating pressure (kPa)	55

The polysaccharide suspension was held in a 5 L feed tank equipped with a stirrer rotating at 500 RPM and was fed to the inlet port of the membrane module by a peristaltic pump (Watson Marlow 323). An identical peristaltic pump was used to draw permeate from the immersed membrane unit. To keep permeate flux constant, subsequent adjustments of the pump velocity were made, measuring the permeate flow and accordingly modifying the pump RPM value.

The TMP was measured by a pressure transducer (PCE-932, PCE Instruments) located at the permeate channel. Experiments were performed at room temperature (20°C), which was monitored using a multiparameter probe (Hanna Instrument, 9828/4). The experimental setup is shown in Figure 3-3.

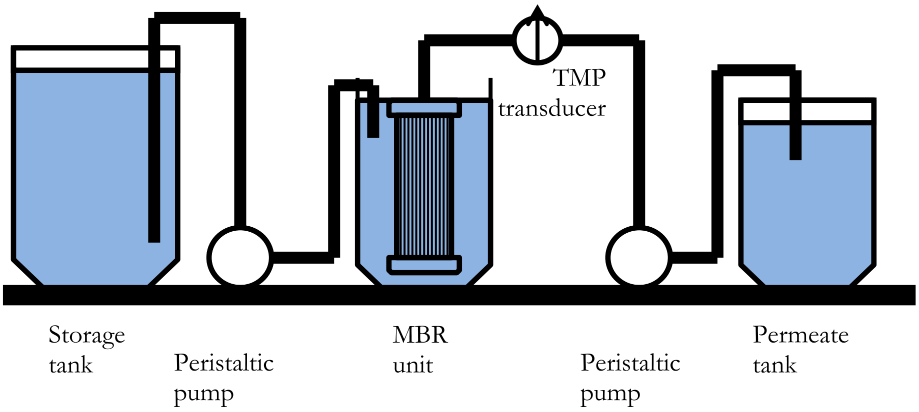

Figure 3-3 - P1 Experimental setup

For P2 and P3, the experimental setup is shown in Figure 3-4. The feed tank was continuously stirred (IKA Eurostar 100) and the wastewater was pumped (MasterFlex L/S, Cole Parmer) to the BEMR unit (Table 3-4) where biological degradation took place. The biological effluent was then sent by gravity to the membrane unit (ZW-1, Zenon GE, US).

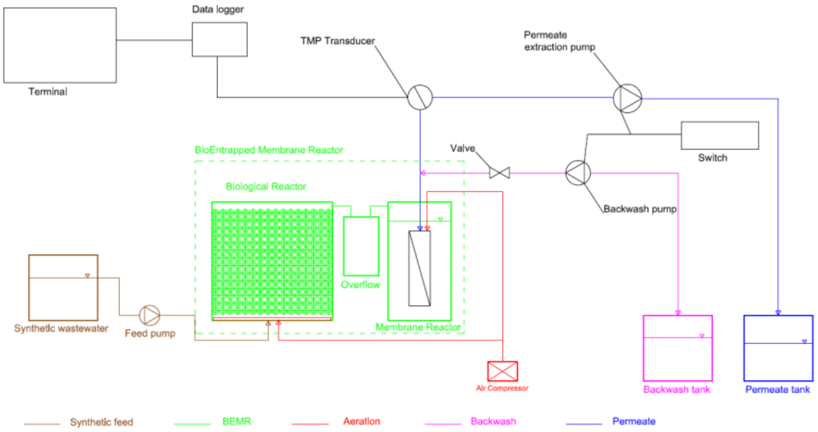

Figure 3-4 - P2-P3 Experimental setup

The TMP was measured using a 0-5 VDC vacuum transducer (PX409, Omega), shown in Figure 3-5.

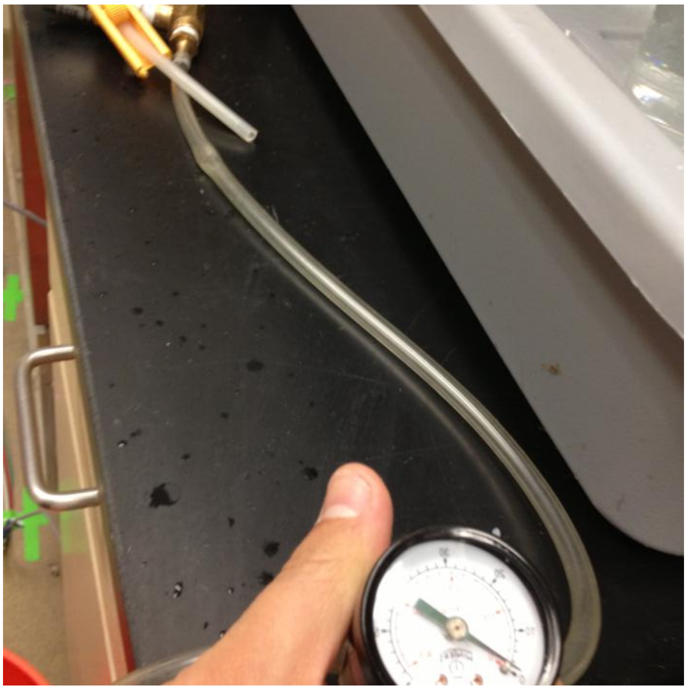

Figure 3-5 - Vacuum transducer PX409 in its calibration phase (using N2)

The vacuum transducer, as well as the set of peristaltic pumps and a DO probe, was connected to a datalogger that is shown in Figure 3-6 (34972A, Agilent) and to a 12V DC power supply (Fisher Scientific).

Figure 3-6 - Agilent 34972A data logger (Agilent Instruments, US)

Table 3-4 - BEMR operational parameters

Parameter	Value	
Carrier diameter	2	in
Total bioreactor volume	14	L
Liquid volume	11.5	L
Dissolved oxygen	8.0 - 9.0	mg/L
Temperature	23±2	°C
pH	6.6 - 6.8	
Flowrate	2	L/h
HRT	06-Dec	h
Permeate flux	20-40	LMH

Both the membrane and the biological reactor were aerated at a constant flowrate through the laboratory air line. The permeate was extracted through a peristaltic pump (MasterFlex L/S, Cole Parmer) regulated according to the desired flux and collected in a tank from which clean water for backwash was withdrawn. The setup is shown in Figure 3-7.

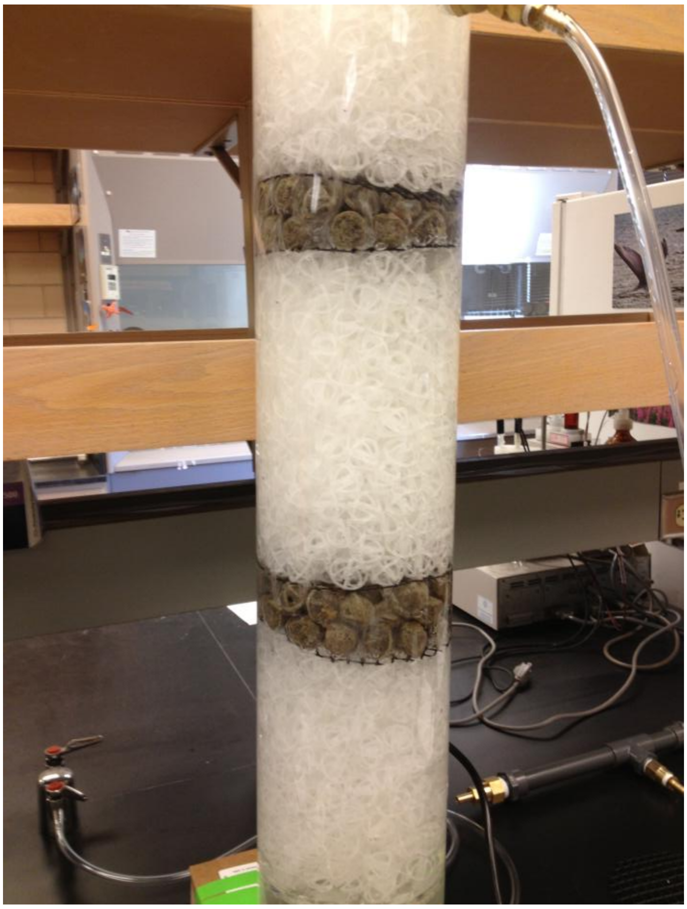

Figure 3-7 - BEMR system: the bioreactor a few moments before starting feeding it

Regular filtration/backwash (F/BW) cycles were set at 29 minutes/1 minute using a programmable switch (Chrontrol XT, Chrontrol), as shown in Figure 3-8, for both the permeate and backwash pump. A PC was connected to the datalogger to record the TMP trend.

Figure 3-8 - Programmable timer for filtration/backwash cycle (Chrontrol XT, Chrontrol US)

Finally, a conventional lab scale MBR has been designed and operated at the University of Salerno, which experimental setup is shown in Figure 3-10. The feed tank was continuously stirred (IKA Eurostar 100) as shown in Figure 3-9, and the wastewater was pumped (Watson Marlow 323U, Watson Marlow) to the oxidation unit (Table 3-5) where biological degradation took place.

Figure 3-9 - Feedtank (50 L) continuously stirred

The biological effluent was then sent by gravity to the membrane unit (ZW-1, Zenon GE, US).

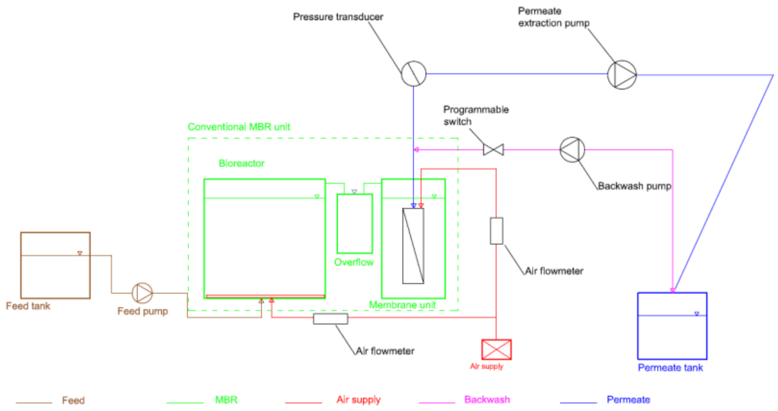

Figure 3-10 – Conventional lab scale MBR experimental setup

The TMP was measured using a 4-20 mA vacuum transducer (PX409, Omega) connected to a datalogger (34972A, Agilent) and to a 0-30V DC power supply (PS-305D, Dazheng) as shown in Figure 3-11.

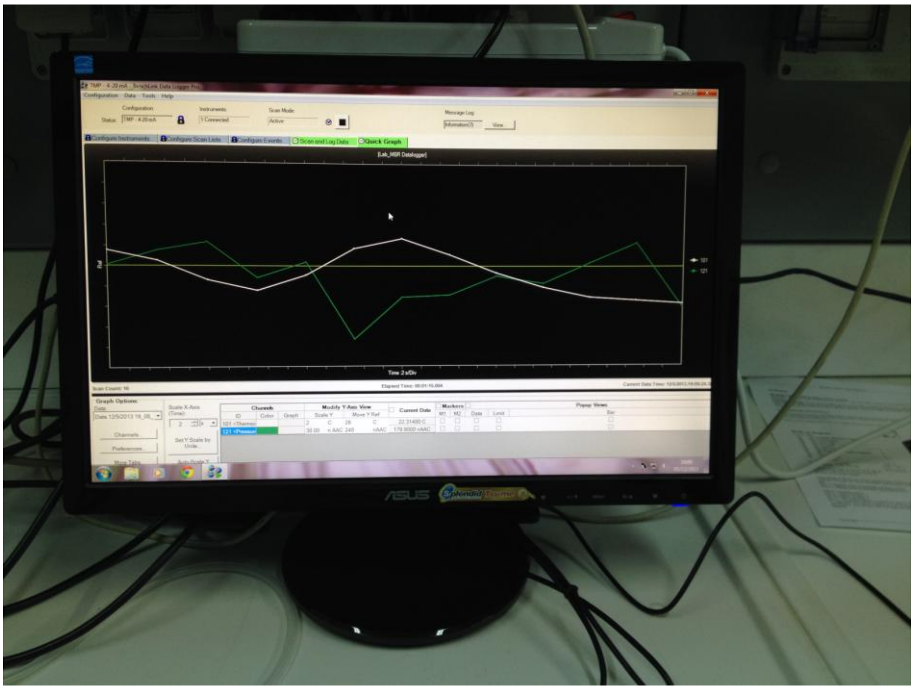

Figure 3-11 - Recording signals through a datalogger

Table 3-5 – Lab scale conventional MBR

Parameter	
HRT	6-12 h
Permeate flux	20-40 LMH
TMP max	55 kPa
Biomass	7000 mg/L
Dissolved Oxygen	7.5 – 8.5 mg/L
Sludge Retention Time	500 d
Biological oxidation volume	8 L
pH	5.2 – 5.8
Temperature	20±3 °C
Filtration/backwash	29 min/1 min

Both the membrane and the biological reactor were aerated at a constant flowrate through the laboratory air line using two flowmeters connected to the datalogger via a JS-46 cable (Figure 3-12).

Figure 3-12 - Air flowmeter connected to the datalogger for recording airflow on both biological and membrane steps (Bronkhorst, US)

The permeate was extracted through a peristaltic pump (qdos30, Watson Marlow) regulated according to the desired flux, and collected in a tank from which clean water for backwash was withdrawn. Regular filtration/backwash (F/BW) cycles were set at 29 minutes/1 minute using a programmable switch (Chrontrol XT, Chrontrol) for both the permeate and backwash pump. A PC was connected to the datalogger to record the TMP trend as well as other parameters such as temperature and air flow. An image of the operating system is shown in Figure 3-13.

Figure 3-13 - P3 experimental setup, composed of a datalogger, a PC, two peristaltic pumps, a UF membrane, a bioreactor and a temporary settler

3.1.3 Biological Reactors

A BEMR and a conventional MBR were set up in the laboratory for experiments in P2 and P3. Each of the MBRs had a working volume of 14 L with a polyvinylidene fluoride (PVDF) hollow fiber UF membrane module installed in it. They were operated separately for about six months each. The BEMR consisted of two compartments, with the first housing the entrapped bio-balls and the second housing the membrane module. The separate compartments allowed each to be designed and operated optimally, as shown in Figure 3-14.

Figure 3-14 - BEMR bioreactor after 3 weeks of operation: biofilm growth can be observed on the internal surface of the reactor

The entrapped bio-balls, 2.5 cm in diameter, were prepared per Yang et al. (2002), and were packed in the BEMR occupying 55% of the first compartment. A bio-ball ready for being fed is shown in Figure 3-15.

Figure 3-15 - A 2.5 cm diameter bio-ball ready for being fed with wastewater

The activated sludge immobilized in the bio-balls of the BEMR and in the conventional MBR was from a municipal wastewater treatment plant (BEMR, Snoqualmie WWTP; conventional MBR, Salerno WWTP). Prior to data collection, the BEMR was operated in batch mode for 20 days to reach a steady-state condition that attained 90% removal of COD (Yu et al., 2009). After steady state was reached in the effluents, membrane modules were installed into the reactors (Figure 3-16).

Figure 3-16 - ZW-1 UF membrane installed and fed with biological effluent; air scouring is in place

Both BEMR and conventional MBR were then operated at varied hydraulic retention times (HRT) of 6, 9, or 12 h during experiments on membrane fouling. The SRT in the BEMR was determined according to Huang et al. (2001). The average SRTs of the BEMR and the conventional MBR were calculated to be 500 d and 20 d, respectively. The MLSS concentration in the conventional MBR was maintained at 8000-9000 mg/L by withdrawal of excess sludge from membrane unit.

3.1.4 Chemicals

TEP were visualized and measured by applying a cationic dye Alcian Blue. The staining solution was prepared with 0.02% of Alcian Blue 8 GX (Sigma Aldrich) in acetic acid buffer solution, maintained at pH 2.5, as shown in Figure 3-17.

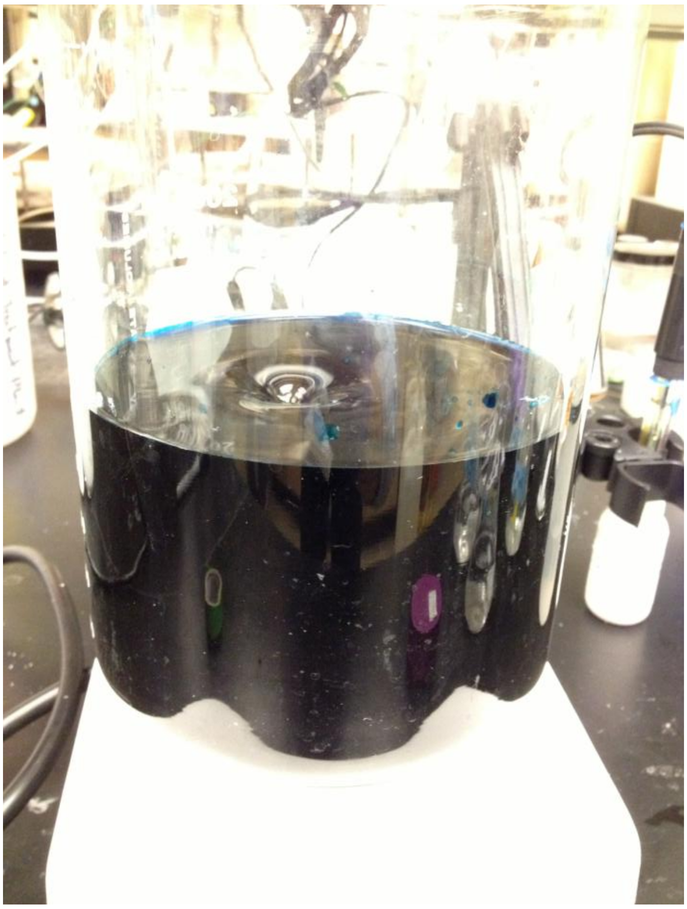

Figure 3-17 - Alcian Blue solution before filtration (Sigma Aldrich, US)

Each batch of staining solution was stored at temperature of 4°C for not more than 4 weeks, as it coagulates over time and a significant reduction of Alcian Blue concentration is likely after pre-filtration (Passow and Alldredge, 1995). Alcian Blue concentrations were monitored by measuring the copper concentration of the staining solution using an atomic absorption spectrometer (Perkin Elmer Analyst 200).

To measure particulate (>0.40 mm) and colloidal (<0.40 mm) TEP, water samples (40–200 ml) were filtered through a series of polycarbonate filters (0.40, 0.20, 0.10 and 0.05 mm pore sizes; 47 mmØ, Whatman Nuclepore) in a glass filter holder, as shown in Figure 3-18.

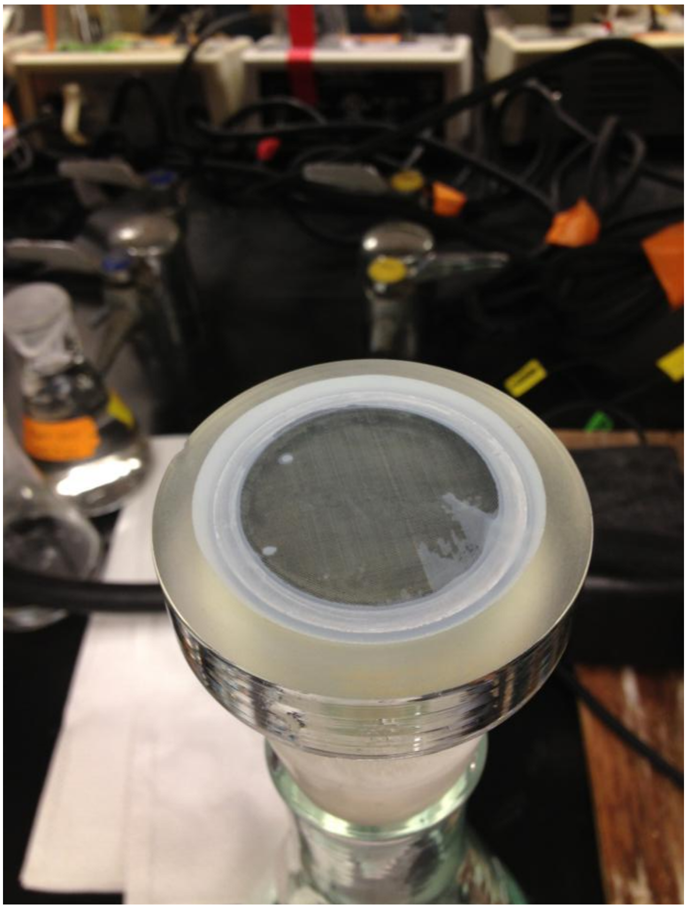

Figure 3-18 - Filtration of samples on a 0.05 μm polycarbonate membrane, and subsequent staining with Alcian Blue

An adjustable pump was installed to maintain a vacuum of 0.2 bars. The accumulated TEP on the filter were stained with 1 ml of pre-filtered

(0.05 mm polycarbonate filter) Alcian Blue solution. The applied dye was allowed to react with TEP for about 10 s. Excess stain was removed by applying low vacuum (<0.2 bar) through the filter and then rinsed by filtering 1 ml of ultra-pure water (milli-Q). The filter was transferred to a 50 ml beaker and then soaked in 6 ml of 80% H_2SO_4 solution for 2 h to elute Alcian Blue that were bound to TEP as well as those adsorbed by the filter (Figure 3-19).

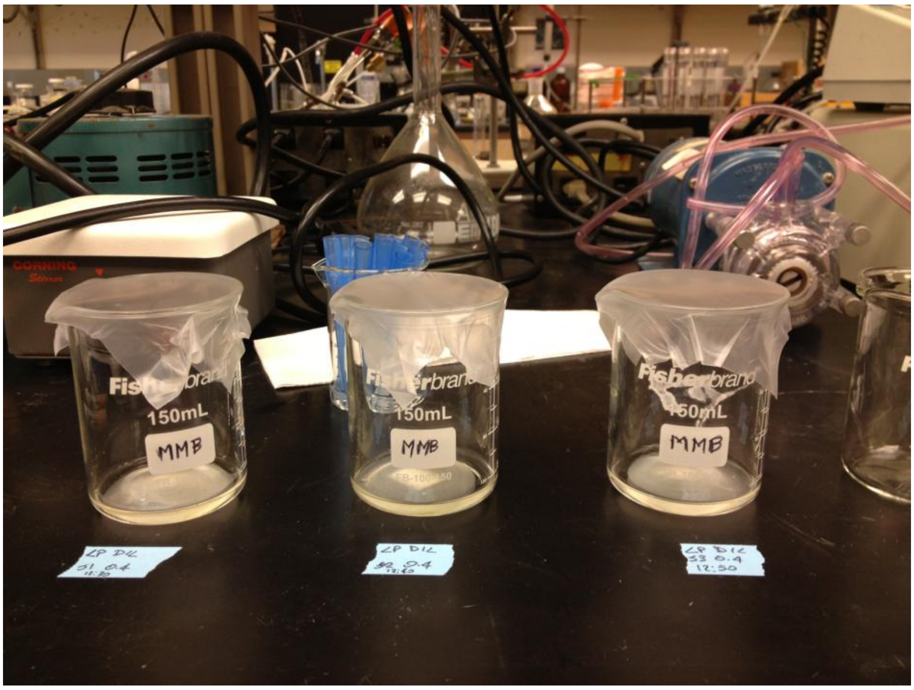

Figure 3-19 - TEP detection: membranes soaking into 80% H_2SO_4 solution to elute Alcian Blue

The beaker was gently swirled 3–5 times within this period. After 2 h, the absorbance of the acid solution was measured using a UV–Vis spectrophotometer (Shimadzu UV-2501PC). Absorbance was measured at 787 nm wavelength using a 1-cm cuvette and ultra-pure water as reference. Two to four replicates were preformed for each water sample.

To prepare bioballs for the BEMR, a mixture of 20 g of 20% (w/v) wet WWTP sludge and 20 mL deionized water was added to 100 mL of 10% (w/v) cellulose triacetate (CTA) (Sigma Aldrich) dissolved in dichloromethane (Sigma Aldrich) and mixed continuously until it was homogeneous. The solution was then poured into plastic carriers to make bioballs of 2 cm in diameter (Figure 3-20).

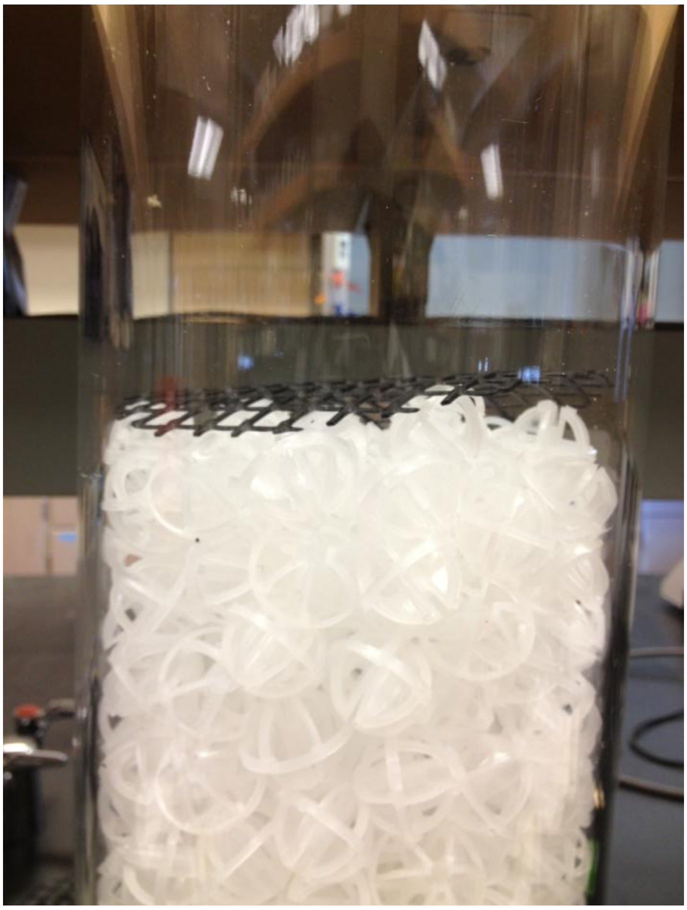

Figure 3-20 - Preparation of the bioreactor with empty plastic carriers to support bio-ball layers

After waiting 20-30 minutes, the bioballs were soaked into a batch reactor filled with a 300 mg/L COD synthetic wastewater for acclimation.

3.2 ANALYTICAL METHODS

3.2.1 COD

COD and sCOD was analyzed daily sampling both the biological effluent and membrane permeate. 10 mL of the sample were added to pre-packed COD vials (Hach Lange) that were subsequently heated at 150°C for 2 hours. The vials were then analyzed through a spectrophotometer (Hach Lange) for the final measurement (Figure 3-21).

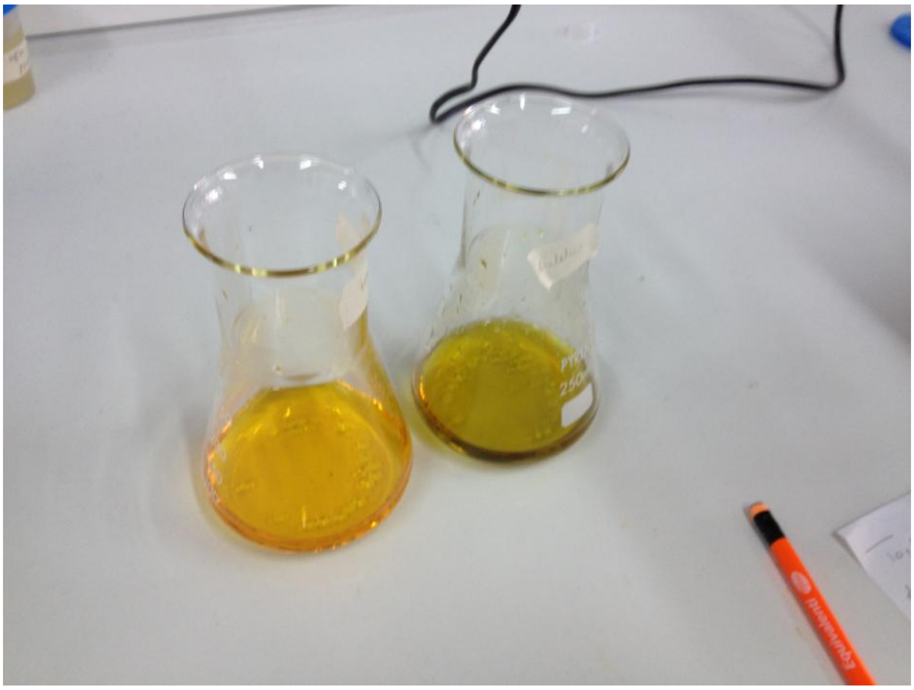

Figure 3-21 - Colorimetric method to analyze COD

3.2.2 Dissolved Oxygen, pH, Temperature

In P2, DO, pH and Temperature of both the bioreactor and the membrane unit were determined daily through a multiprobe system (SevenGo, Mettler). In the conventional lab scale MBR, DO and pH of both the bioreactor and the membrane unit were determined daily through a multiprobe system (HI 9828, Hanna). Water temperature of the bioreactor was monitored through a K-type thermocouple connected to the datalogger.

3.2.3 Solids

To determine total solids (TS) a clean dish was heated for 1 hour at 103-105°C. The dish was then removed from the drying oven and placed in a desiccator until needed. The cooled dish was then immediately weighed. Once selected a sample volume that would yield between 2.5 and 200 mg of solids, the sample was well mixed and measured into a graduated cylinder to the selected volume. The measured volume was then poured into the preweighed dish. Having rinsed any residue from the graduated cylinder into the evaporating dish with a small amount of distilled water, the dish was therefore put to evaporate to dryness in a drying oven at 98°C. Once the evaporated dish was dry - after at least 1 hour at 103-105°C – the dish was removed from drying oven and cool in a desiccator to room temperature. The dish-residue was weighed and final value recorded (Figure 3-22).

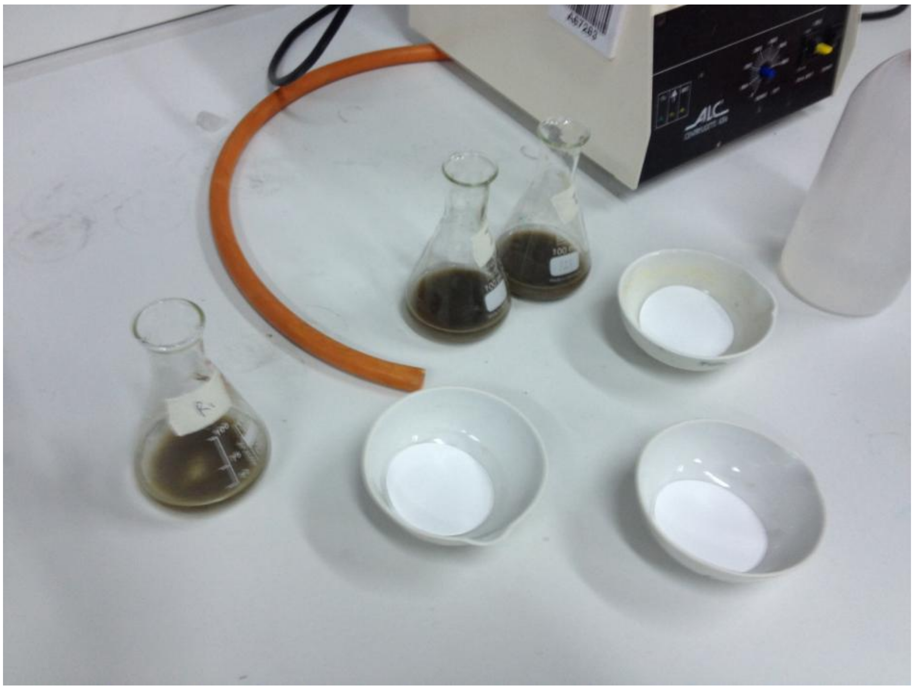

Figure 3-22 - Determination of Total Solids in the biological reactor through membrane filtration

The procedure was repeated until a constant weight was obtained or until the weight loss was less than 0.5 mg or 4% of previous weight.

3.2.4 TEP measurement

TEP is measured spectrophotometrically using Alcian blue, a cationic dye that binds to acidic mucopolysaccharides. For the measurement of exopolysaccharides concentration in wastewater, the phenol method of Dubois et al. (Dubois et al., 1956) requires concentrated acid to break all the carbohydrates into monosaccharides, which are subsequently measured spectrophotometrically using glucose as standard for the calibration. The whole analysis takes about one hour and involves sulphuric acid, which makes the method rather tedious. Besides, it has been found that high concentrations of nitrite and nitrate disturb the analytical method so that the obtained polysaccharide concentrations must be readjusted using a correction equation (Drews et al., 2007). Therefore, the method used for TEP analysis offers various advantages over the conventional method for polysaccharide analysis in MBR fouling research: it is simpler and quicker, the dye is non-toxic and no strong acids are used (de la Torre et al., 2008). TEP measurements were based on the spectrophotometric method introduced by Passow and Alldredge in 1995. In this method, the samples are filtered through polycarbonate filters with pore size of 0.4 mm. The accumulated TEP on the filters were subsequently stained with Alcian Blue. TEP were semiquantified spectrophotometrically based on a calibration with the standard polysaccharide Gum Xanthan. In this study, the existing method was expanded by filtering the filtrate samples through a series of filters having pores of 0.4 and 0.05 mm.

TEP were visualized and measured by applying a cationic dye Alcian Blue. The staining solution was prepared with 0.02% of Alcian Blue 8 GX (Sigma Aldrich) in acetic acid buffer solution, maintained at pH 2.5. Each batch of staining solution was stored at temperature of 4°C for not more than 4 weeks, as it coagulates over time and a significant reduction of Alcian Blue concentration is likely after pre-filtration (Passow and Alldredge, 1995). The Alcian Blue concentrations were monitored by measuring the copper content of the staining solution using an atomic absorption spectrometer (Perkin Elmer AAnalyst 200). The Alcian concentration was computed based on the mass proportion of copper in each Alcian Blue molecule ($C_{56}H_{68}Cl_4CuN_{16}S_4$).

To measure particulate (>0.40 mm) and colloidal (<0.40 mm) TEP, water samples (40–200 ml) were filtered through a series of polycarbonate filters (0.40, 0.20, 0.10 and 0.05 mmpore sizes; 47 mmØ, Whatman Nuclepore) in a glass filter holder. An adjustable pump was installed to maintain a vacuum of 0.2 bars. The accumulated TEP on the filter were stained with 1 ml of pre-filtered (0.05 mm polycarbonate filter) Alcian Blue solution. The applied dye was allowed to react with TEP for about 10 s. Excess stain was removed by applying low vacuum (<0.2 bar) through the filter and then rinsed by filtering 1 ml of ultra-pure water (milli-Q). The filter was transferred to a 50 ml beaker and then soaked in 6 ml of 80% H_2SO_4 solution for 2 h to elute Alcian Blue that were bound to TEP as well as those adsorbed by the filter. The beaker was gently swirled 3–5 times within this period. After 2 h, the absorbance of the acid solution was measured using a UV–Vis spectrophotometer (Shimadzu UV-2501PC). Absorbance was measured at 787 nm wavelength using a 1-cm cuvette and ultra-pure water as reference. Two to four replicates were preformed for each water sample. Absorbance corrections due to stain adsorption on filter media and in some cases interference due to high turbidity were also determined. Filter media adsorbs significant amount of Alcian Blue during TEP staining while some suspended solids in water samples could not be totally oxidized by sulphuric acid and may subsequently interfere with the absorbance measurements. The filter blank was prepared by staining a clean filter with Alcian Blue. For turbidity correction, suspended solids in turbid water samples (same sample volume in TEP measurement) were retained in 0.4 mm pore size filters without subsequent staining. Both filter blank and turbidity filters were soaked in sulphuric acid for 2 h, following the previously mentioned procedure until absorbance measurements. Typical ranges of filter blank absorbance were between 0.08 and 0.11 for 0.4 mm polycarbonate filters and 0.09 and 0.12 for 0.05 mm polycarbonate filters. Turbidity correction was not necessary for most of the samples but it was significant in some cases, especially in raw water samples. Turbidity correction is normally below 0.20; otherwise, the filtered sample volume was reduced to a level that would minimize retention of solid particles. To compute the net absorbance of stain eluted from TEP, corrections due to turbidity (T787) and filter blank (B787) were subtracted from the sample absorbance (A787). TEP concentrations were then computed in terms of Xanthan equivalent per liter by multiplying the net absorbance with a calibration factor (fx) following the equation:

$$TEP = \frac{f_x}{V_f}(A_{787} - B_{787} - T_{787})$$

where A_{787} is the absorbance of the stain eluted from TEP and the filter; B_{787} is the average absorbance of stain eluted from blank filters; T_{787} is the absorbance correction due to turbidity; f_x is the calibration factor in mg Xanthan equivalent (X_{eq}) per unit absorbance at 787 nm (based on Passow and Alldredge, 1995); and V_f is the filtered volume of the sample in liters.

The TEP calibration curve is shown in Figure 3-23.

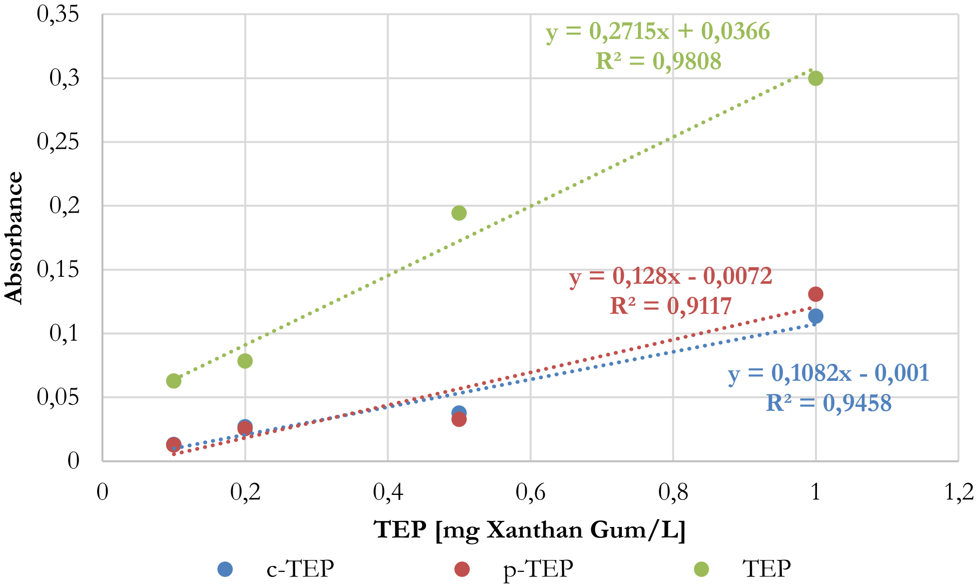

Figure 3-23 - Calibration curve for p-TEP, c-TEP and TEP

Concentrations of TEP fractions were based on serial filtration using different pore size filters. Particulate TEP or p-TEP refers to TEP retained on 0.4 mm polycarbonate filters while colloidal TEP or c-TEP refers to TEP that passed through 0.4 mm polycarbonate filters but retained on 0.05 mm polycarbonate filters. Passow (2000) reported part of c-TEP as dissolved TEP precursors (<0.2 mm) while Verdugo et al. (2004) considered it as hydrogels. In order to be consistent with the IUPAC definition of colloidal substances (0.001–1 mm), this fraction was referred to in this study as “colloidal” rather than “dissolved”.

4 RESULTS AND DISCUSSION

In the present chapter, results of the three research phases are presented and discussed. More in depth, for P1 results are presented in terms of TMP trends during filtration tests in which nanospheres have been added, and a numerical model has been developed in order to link nanospheres addition to total resistance of the hybrid layer.

For P2, results are shown in terms of organic matter removal (as COD), TMP trends, and HRT dependence of pressure behaviors, as well as TMP-Temperature link.

Finally, for P3 results are shown in terms of TEP analysis and occurrence in a BEMR system and their subsequent removal through physical filtration.

4.1 PHASE 1 – NANOMATERIALS

Filtration experiments were performed at first with sodium alginate solutions according to the procedure described in the previous chapter.

After 180 minutes of filtration at 20 LMH the TMP attains a value of roughly 0,9 bar, indicating severe membrane fouling. This observation is in line with the common assessment in the literature that polysaccharides are potentially one of the most significant fouling species in wastewaters and natural waters. Similar behavior has been observed with other types of organic foulants as well as colloidal particles. It has to be noted that flux recovery after the chemical cleaning is almost complete. This result is in line with previous findings regarding sodium alginate fouling in MBRs. During filtration of the synthetic solution, sodium alginate deposition on the membrane led to highly compressible fouling. This material was also easily removed through chemical cleaning and backwashing.

4.1.1 Effect of nanoparticles addition on filtration

Once assessed the behavior of sodium alginate in terms of TMP increase, the nanospheres have been added to the MBR unit during the filtration of the synthetic solution in order to check whether the cake resistance could be reduced (Teychene et al., 2011). A sharp decrease of the TMP trend has been confirmed for each investigated diameter, as shown in Figure 4-1.

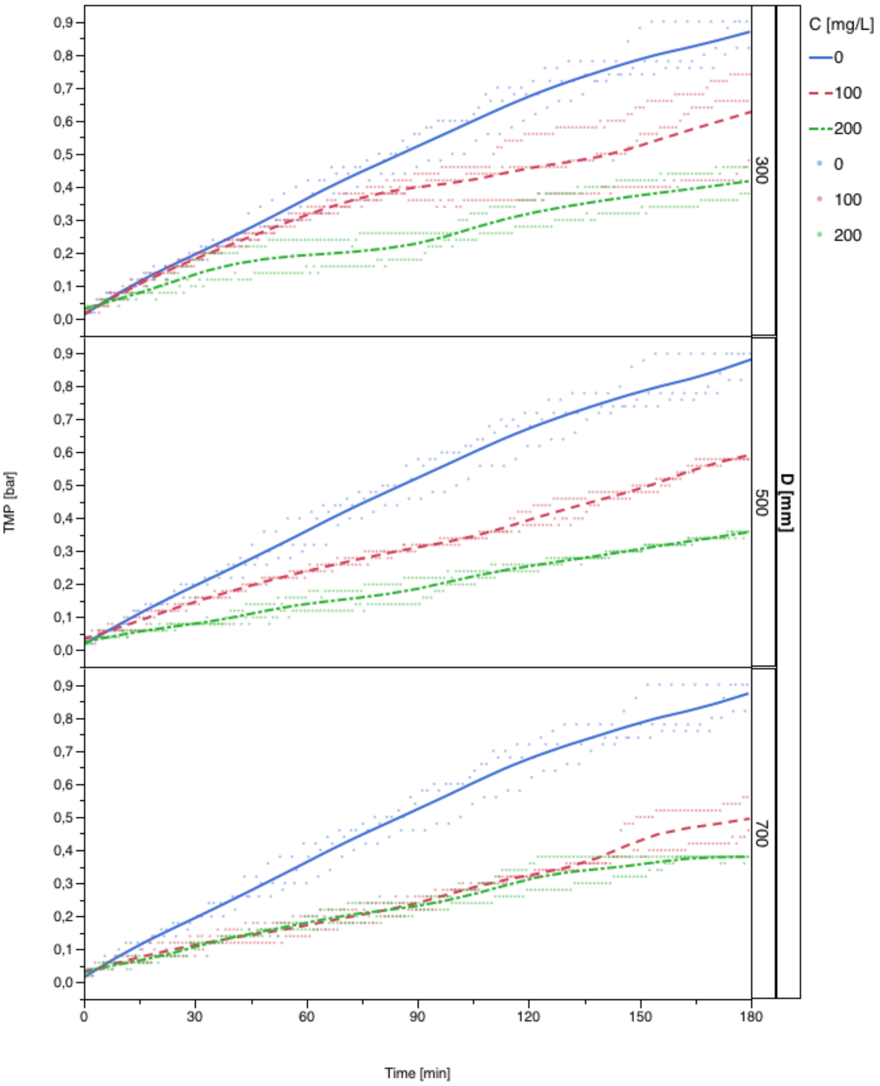

Figure 4-1 - TMP trends at different nanospheres concentrations during the filtration of a synthetic solution containing sodium alginate (20 mg/L as D-glucose)

From the analysis of the TMP trends, it can be inferred that the addition of nanoparticles reduced the pressure required over time to allow the filtration of a fixed permeate flow (20 LMH). The maximum reduction in TMP after a filtration time of 180 minutes was attained using the maximum diameter (700 nm) at the highest concentration (200 mg/L). It must be noted that both diameter and concentration play a major role in cake resistance reduction, and therefore in limiting TMP increase over time. According to the results, the presence of nanospheres engineers the cake layer structure – more specifically, its compressibility – and makes the fouling layer become less compressible. This is also confirmed by geometrical considerations, as the 100 mg/L concentration provided a layer thickness of 8,45 μm under the hypothesis that all the nanoparticles were deposited onto the membrane; the same approach was pursued for the 200 mg/L concentration, which led to a nanospheres layer thickness of 17,07 μm.

Specific TMP trends are shown in Figure 4-2 for 300 nm particles. After 180 minutes, a concentration of 200 mg/L helped achieving more than 50% TMP reduction.

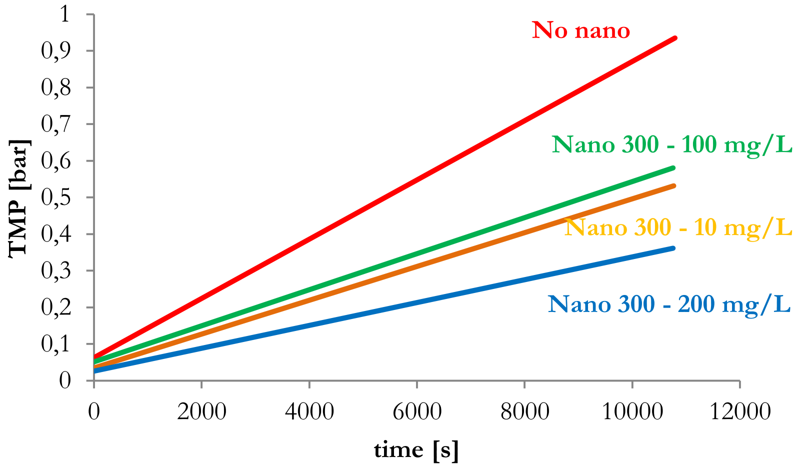

Figure 4-2 - Comparison of TMP trends with and without 300 nm nanospheres, at different concentrations

Similarly, TMP trends are shown in Figure 4-3 for 500 nm nanospheres, which show almost identical behavior, but a slightly better TMP reduction recorded when higher concentrations of nanoparticles are dosed.

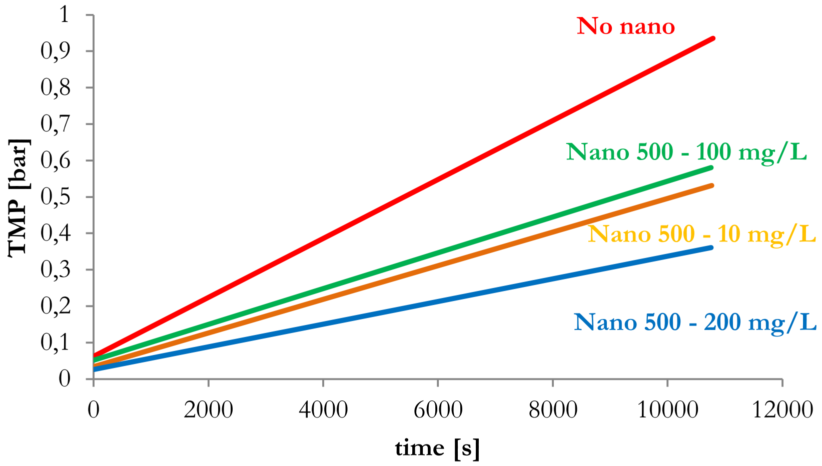

Figure 4-3 - Comparison of TMP trends with and without 500 nm nanospheres, at different concentrations

Figure 4-4 shows TMP trends when 700 nm nanospheres are employed. This set of experiments returned the best results in terms of membrane fouling control, which is in line with the findings proposed by the implementation of the numerical model, as reported below.

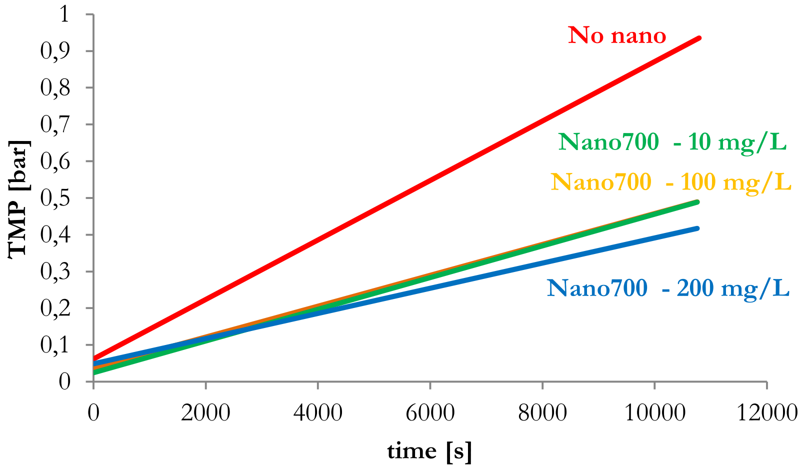

Figure 4-4 - Comparison of TMP trends with and without 700 nm nanospheres, at different concentrations

Finally, the size distribution of the sodium alginate solution is shown in Figure 4-5. The polysaccharide presented a mean dimension during the experiment (180 minutes) of 213 nm.

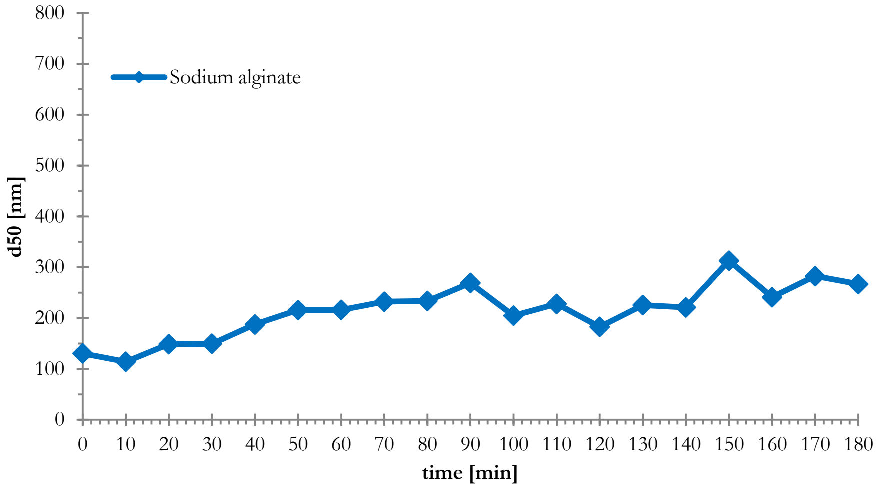

Figure 4-5 - Sodium alginate d_{50} [nm] over time in the lab scale membrane reactor

This indicates a tendency to occlude all the pores at the top of the nanoparticles layer when nanospheres with a diameter of 300 nm are added, since r=130 nm. On the opposite, larger diameters allow sodium alginate filtration through the nanosphere layer, limiting the TMP increase. This means, in turn, that lower compressibility values are attained when thicker nanospheres layers are formed onto the membrane.

4.1.2 Filtration model

In order to determine the resistance due to the membrane (R_m), a set of filtration tests has been performed using only deionized water. The corresponding resistance ($R=R_m$) was equal to:

$$R = \frac{TMP}{J\mu_w}$$

Where J is the flux, μ_w represents the dynamic viscosity of the water and TMP is the monitored pressure. The resulting R_m was equal to 1.8 x 10^{11} m^{-1}. This value is in accordance with other published studies (Ng and Kim, 2008).

A set of preliminary filtration tests dosing nanospheres in deionized water and performed at a constant flux of 20 LMH, showed that the particle arrays induced an initial permeate flux decline not depending on the particle size or concentration; then, the TMP trend kept steady.

The contribution in terms of resistance due to the addition of nanoparticles has been evaluated through filtration of deionized water in which nanospheres (300, 500 or 700 nm) at different concentration (100 or 200 mg/L) were dosed in the membrane module. Resulting TMP trends showed the same resistance, due to the fact that after a few seconds a steady value for TMP was attained (0,06 bar).

Regardless of the diameter used, no difference in terms of TMP increase was observed. Moreover, at the same deposited mass (100 or 200 mg/L) each particle type showed the same behavior in terms of resistance. Therefore, it can be argued that TMP has no effect on the nanospheres layer resistance, since the formed layer is non-compressible. The flux recovery after membrane cleaning is complete when deionized water is filtered dosing nanospheres.

The resulting resistance (R_n), obtained from the previously explained equation in which $R=R_m+R_n$, is then equal to 5,4 x 10^{11} m^{-1} for each tested diameter and concentration. This is probably because the pores of the nanospheres layer are almost equal in terms of mean diameter, and therefore no variation in resistance has been reported for deionized water filtration.

In a previous study (Ng and Kim, 2008), Authors applied a sectional approach to account for the uneven cake formation in determining total filtration resistance. The Authors divided the membrane surface into equal fractional areas, and calculated separate total resistances, R, for each section, which can consist of constant resistance R_0 – due to membrane resistance R_m and nanoparticles layer resistance R_n – and time-dependant resistance due to cake formation, $\varkappa t$. The total resistance in each section is then described as:

$$R = R_0 + \kappa t$$

Where $\varkappa$ is a parameter depending on both nanospheres diameter and concentration. R_0 is equal to R_m when no nanospheres are added, while in the opposite case $R_0=R_m+R_n$.

The sectional resistance model was developed using a partially analytic approach. By dividing the membrane into sections and considering the resistance in each section, the model accounts for uneven cake formation stemming from varying shear distribution along the membrane. Previous studies (Guglielmi et al., 2007; Bolton et al., 2006; Gander et al., 2000) were conducted using a submerged MBR, which filtered glucose-based synthetic wastewater using different sludge concentrations, filtration fluxes, and aeration intensities, and a similar model was employed. Comparison of the measured and computer-simulated transmembrane pressure over MBR operation time revealed that the model is able of capturing general trends and modeling of membrane fouling phenomenon.

From the comparison of the model with the P1 experimental results, it has been possible to determine the value of $\varkappa$ as introduced in the model. In Table 4-1 the comparison between experimental results and developed model is reported in terms of R^2, from which it can be inferred that the model properly fits and can forecast TMP trends over time.

Table 4-1 - Model/experimental results comparison and R^2 for each tested combination

			D ***[nm]***			
		R^2	**0**	**300**	**500**	**700**
		0	0,991	-	-	-
C	***[mg/L]***	**100**	-	0,921	0,983	0,968
		200	-	0,942	0,984	0,971

In Figure 4-6 results in terms of $\varkappa/\varkappa_0$, $\varkappa_0$ being the empirical parameter when no nanospheres are added, are reported in function of nanoparticle diameter and used concentration.

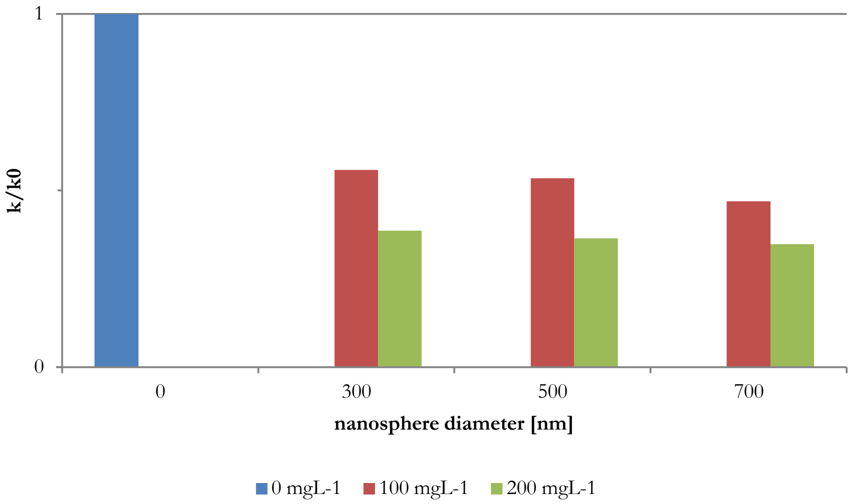

Figure 4-6 - Values of $\varkappa/\varkappa_0$ in function of both nanoparticle diameter and concentration, $\varkappa_0$ being the parameter for the experiment without nanospheres addition

It can be observed that there is a direct correlation between TMP reduction and both nanospheres concentration and diameter: higher concentrations and larger nanospheres led to better filtration performance, in that larger pores allowed sodium alginate to filter through the engineered layer.

A decrease in $\varkappa$ – and therefore in cake resistance – is reported when a concentration of 200 mg/L is added to the membrane unit. This could be explained by the fact that the thickness of the layer played a major role in the filtration process, whatever the mean diameter of the nanosphere may be. Moreover, the cake resistance is influenced by the pore size, in that higher diameters led to a stronger decrease in TMP.

4.2 PHASE 2 – BEMR

In the phase discussed below, experiments were run testing a synthetic wastewater with a 300 mg/L COD. The whole phase has been developed at the Civil and Environmental Engineering Department of the University of Washington (US). A BioEntrapped Membrane Reactor (BEMR) has been operated for 6 months, in order to analyze fouling rate, COD removal, HRT and temperature influence on membrane fouling.

4.2.1 COD removed through biological oxidation and membrane filtration

COD removal has been assessed daily on both the biological effluent and the membrane permeate. While complete COD removal (99%) was achieved over time through membrane filtration, different removal rates were achieved through biological oxidation, as shown in Figure 4-7. Over time, 50% to 90% COD removal was achieved after the biodegradation step. In addition, soluble COD (sCOD) has been analyzed in samples collected from the bioreactor effluent, in which an almost (average 95%) complete sCOD removal was achieved. Therefore, it was inferred that the COD fraction due to wastewater was almost completely removed by the bioreactor. On the other hand, a small fraction of detached biomass was present in the biological effluent, contributing to a higher COD value.

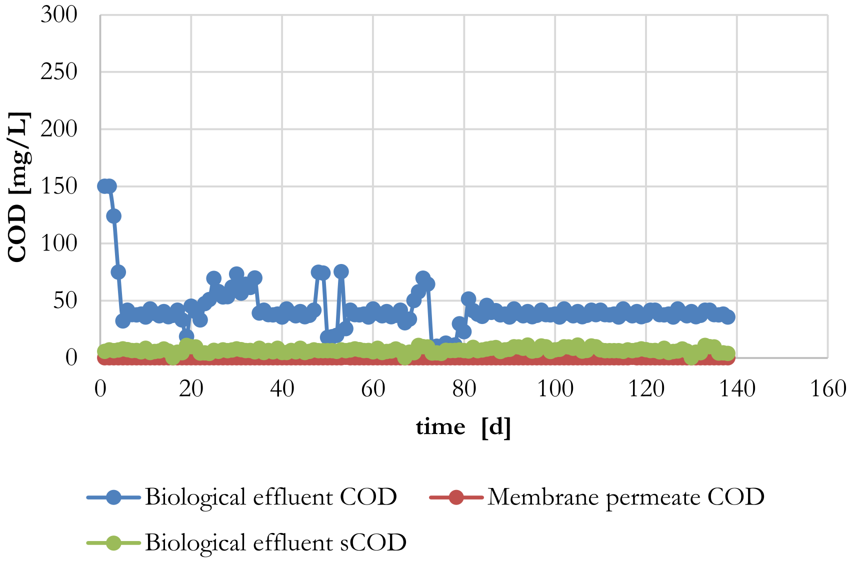

Figure 4-7 - COD and sCOD removal after biological degradation and membrane filtration

4.2.2 Analysis of membrane fouling at different HRT

Membrane fouling rate was analyzed in terms of TMP trends at different HRTs (6-12 h) in the BEMR system for a total of six months of operation. Different HRTs led to a different development of biomass in the reactor and longer HRTs caused lower COD removal rates.

COD removal in the bioreactor slightly decreased with decreasing HRT, but total efficiency could be easily kept over 90% regardless of HRT. DO and Specific Oxygen Uptake Rate (SOUR) slightly decreased as HRT decreased from 12 to 6 hours. This could be explained by impeded transfer rate of both substrate and oxygen due to high MLSS (11 g/L) concentration and sludge viscosity.

The low HRT would result in high TEP concentrations and sludge viscosity. These factors had negative effect on membrane fouling. Therefore, too low HRT may have a negative effect on membrane permeate flux. The low HRT could cause excessive growth of filamentous bacteria. Filamentous bacteria had great impacts on the performance of MBR systems because it led to more release of EPS and TEP, higher sludge viscosity and irregular shaped flocs. Filamentous bacteria used as the fixing type of adhering the membrane fouling material to increase the clinging intensity of the membrane foulants. As shown in the present chapter, MLSS concentration, TEP, sludge viscosity, and filamentous bacteria had strong impacts on membrane fouling behavior.

Sludge viscosity is an important factor that affects the hydrodynamic conditions of MBRs. The cross-flow velocity of sludge suspension decreased sharply as sludge viscosity ranged between 0.95 and 1.05 cP. Even though results showed that HRT had little influence on irreversible fouling, it has an important impact on design and in terms of fouling development rates, which could also influence cleaning protocols and operational expenses.

4.2.3 Effect of permeate flux on fouling development rate

It is clearly expected that water permeation through the membrane would cause rapid formation of a fouling layer due to compulsive transport of foulants into the membrane surface by the drag force of permeate flow, resulting in clogging membrane pores and building up the fouling layer. It is well known that permeation drag is a dominant force affecting the initial attachment of feed components onto the membrane surface. By conducting comparative experiments with and without permeate flux, Ognier et al. (2004) concluded that the presence of permeate flux caused highly irreversible fouling and that filtration resistance by foulants adsorption in the absence of permeate flux was very small. As a result, because such an adsorption test without water permeation might not represent the true fouling tendency of membranes in real applications, it is required to investigate the role of the presence of permeate flux on membrane fouling. Moreover, there have been only few research studies addressing the effect of operational conditions such as permeate flux and tangential flow as well as the influent properties such as feed composition and strength on fouling in terms of those subdivided filtration resistances.

Permeate flux effect on fouling rate has been assessed, operating the BEMR at 20, 30 and 40 LMH. In this chapter, results are discussed for a HRT of 6 hours.

Figure 4-8 shows the TMP trend for a 20 LMH test, in which a total volume of 1010 L has been treated over 3 weeks of operation, before a maximum value for TMP was achieved, which required chemical cleaning to take place.

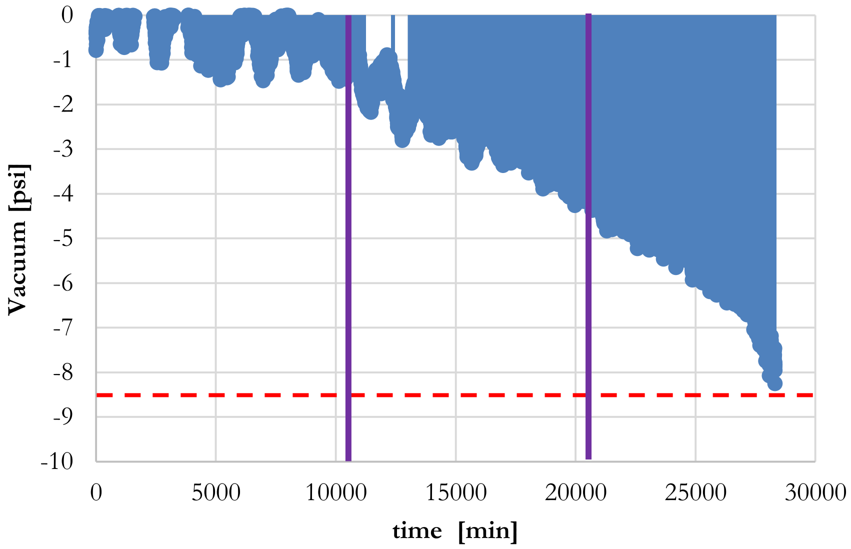

Figure 4-8 - TMP trend for a 6 h HRT and at 20 LMH

Figure 4-9 shows the TMP trend for a 30 LMH test, in which a total volume of 467 L has been treated over 2 weeks of operation, before a maximum value for TMP was achieved, which required chemical cleaning to take place.

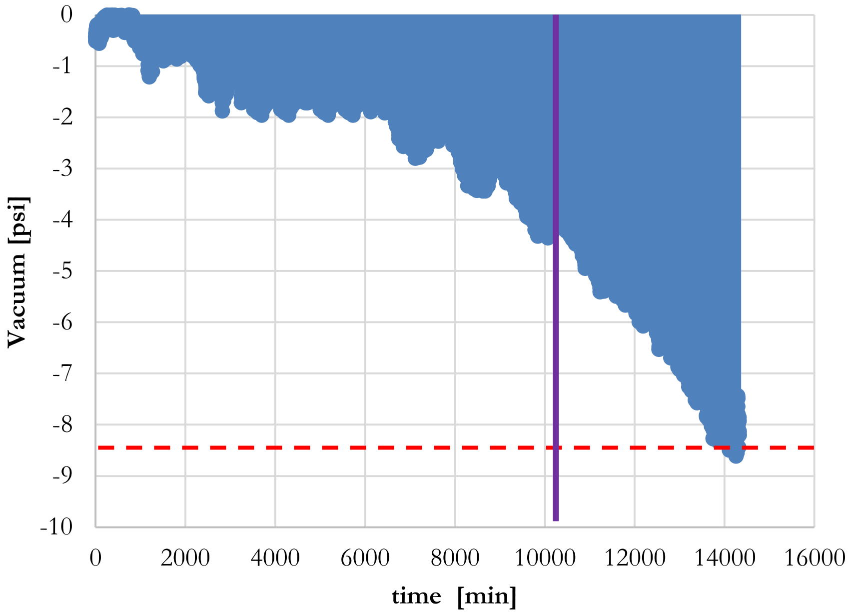

Figure 4-9 - TMP trend for a 6 h HRT and at 30 LMH

Figure 4-10 shows the TMP trend for a 40 LMH test, in which a total volume of 300 L has been treated over 1 week of operation, before a maximum value for TMP was achieved, which required chemical cleaning to take place.

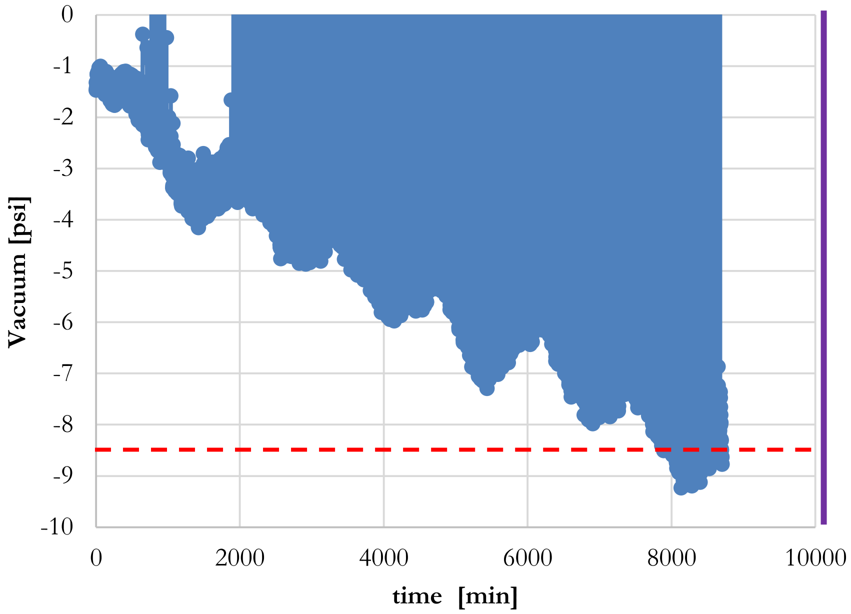

Figure 4-10 - TMP trend for a 6 h HRT and at 40 LMH

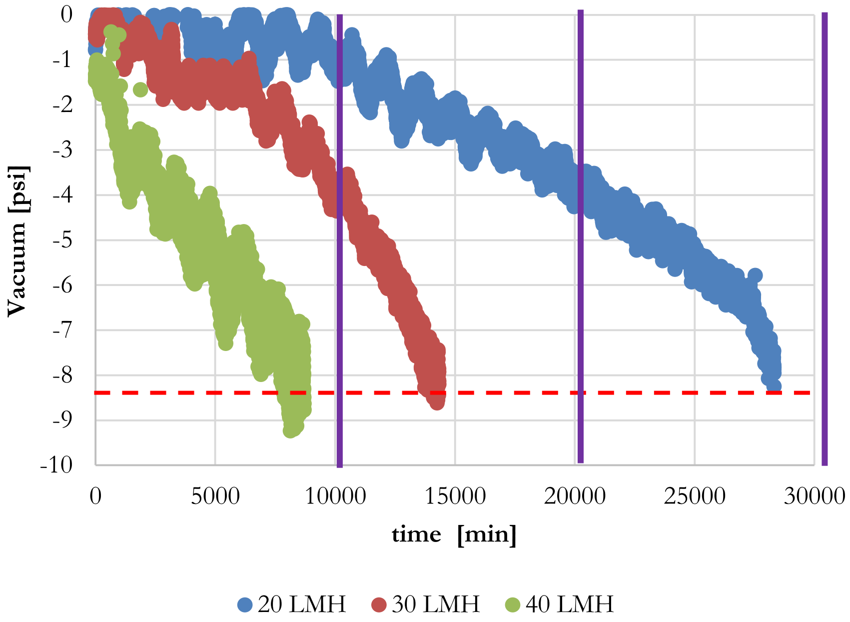

Figure 4-11 - Comparison of TMP trends at different permeate fluxes in a BEMR

Figure 4-11 shows different permeate fluxes in terms of TMP trends, and it can be inferred a predisposition for the BEMR to operate more smoothly at lower permeate fluxes. A plateau – in terms of TMP levels – was reached for both the 20 and 30 LMH tests after the second day of filtration, and until day five, after which fouling increased and TMP soared. This behavior was not observed at 40 LMH, because of the accelerated development of membrane fouling, which eventually led to high (i.e. 3 to 4 psi as vacuum) TMP levels after only a few hours. As discussed elsewhere, while COD removal kept steady independently of the permeate flux, TEP levels climbed sharply inside the membrane reactor as soon as permeate flux increased. This can be explained by the lower HRT, which forced biodegradation byproducts to leave the bioreactor sooner, and therefore polysaccharides could not be completely degraded, eventually accumulating at the membrane filtration phase (Sun et al., 2006). In addition, higher permeate flux values emphasized daily fluctuations in TMP levels due to changes in temperature, and therefore in viscosity. This aspect has been discussed further in the paragraph below.

Similarly, experiments at 20, 30 and 40 LMH have been reported in terms of TMP vs. VSP (Figure 4-12, Figure 4-13 and Figure 4-14, respectively). From those graphs becomes even more evident the improved performance of the BEMR system operated at lower permeate fluxes.

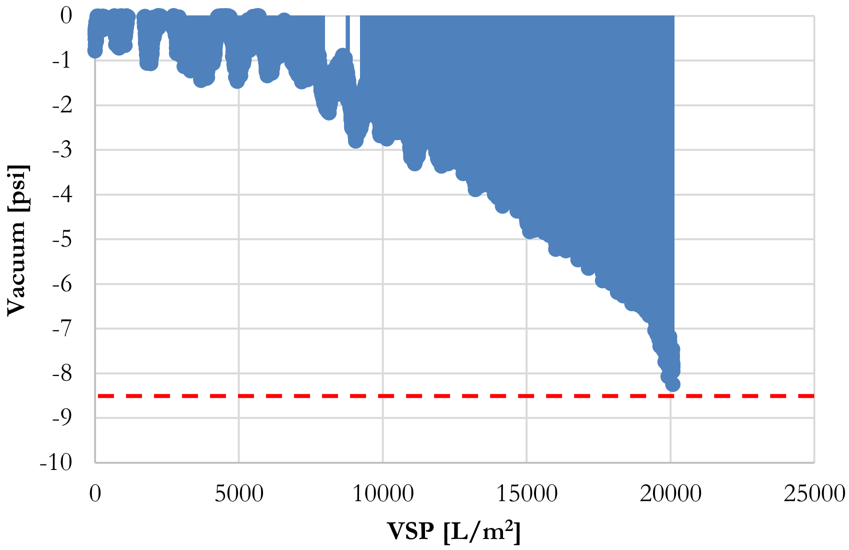

Figure 4-12 - Experiment at 20 LMH: TMP vs VSP

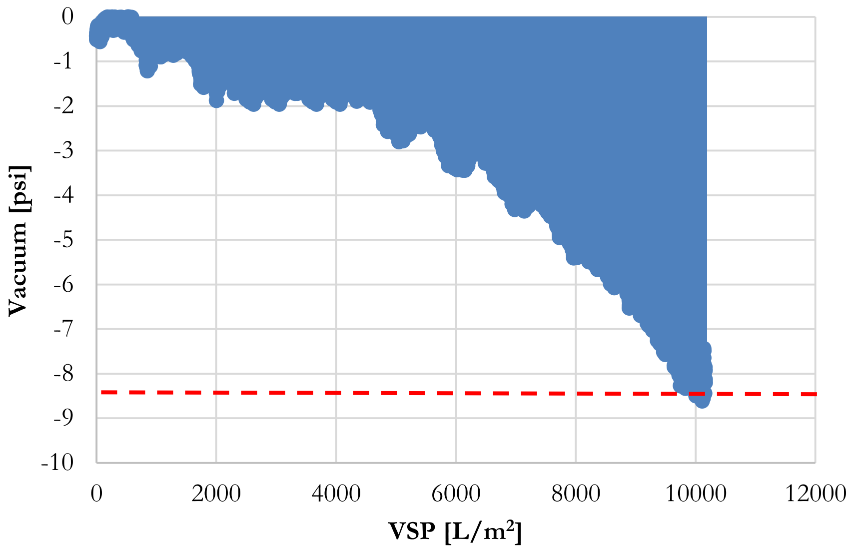

Figure 4-13 - Experiment at 30 LMH: TMP vs VSP

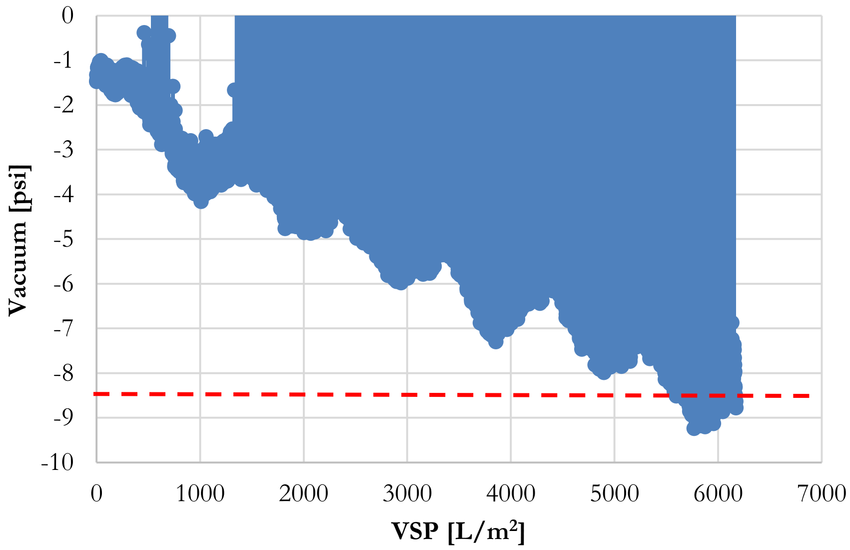

Figure 4-14 - Experiment at 40 LMH: TMP vs VSP

4.2.4 Effect of temperature on fouling development rate

Flux is inversely proportional to the viscosity of the permeate passing through the membrane pore, if all other conditions including TMP and filtration resistances stay constant. Since the MBR permeate has little dissolved materials, its viscosity is virtually same as that of clean water.

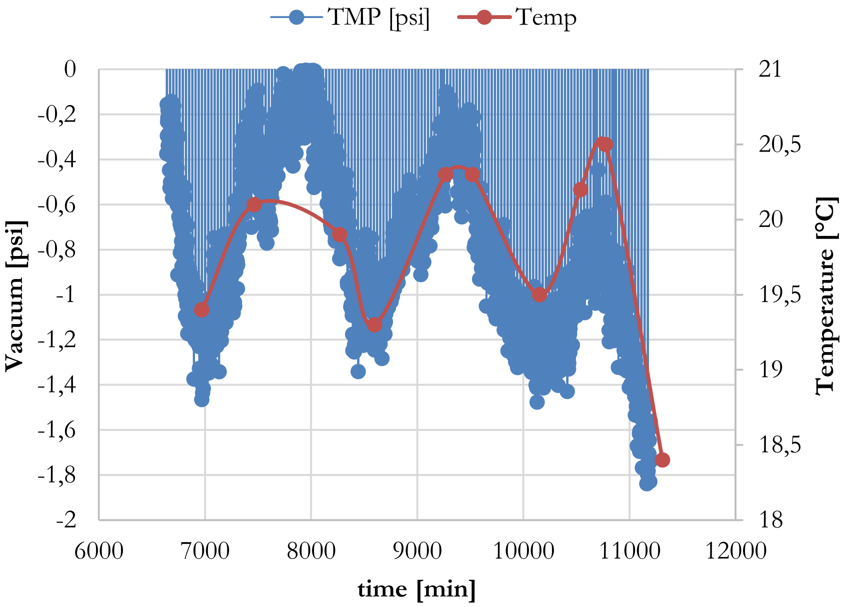

Figure 4-15 - Temperature effect on viscosity and TMP

Based on the relation between flux and viscosity, flux can be corrected against a reference temperature for trending the true membrane flux. Typically, flux is corrected against 20°C using the following equations based on the normalized viscosity.

$$\mu_T = -9.802 \times 10^{-6} T^3 + 1.130 \times 10^{-3} T^2 - 5.793 \times 10^{-2} T + 1.785$$

$$J_{T_0} = \frac{\mu_T}{\mu_{T_0}}$$

where:

μ_T : Water viscosity at current temperature (cP);
μ_{T0} : Water viscosity at reference temperature (cP);
J : Flux observed (LMH);
J_{T0} : Flux at reference temperature(LMH);
T : Water temperature (°C);
T_0 : Reference temperature (°C).

Alternative equation is also available (Wilde, 2007):

$$J_{T_0} = J\left(\frac{42.5 + T_0}{42.5 + T}\right)^{1.5}$$

where:

J : Flux observed (LMH);
J_{T0} : Flux at reference temperature(LMH);
T : Water temperature (°C);
T_0 : Reference temperature (°C).

Although above correction method is widely used to trend membrane flux, it has a significant limitation especially in MBR. The equation counts in permeate viscosity effects in membrane pores, but mixed liquor viscosity, biological activity, oxygen transfer efficiency, and even microbial metabolism can change at different temperatures. For instance, at low temperature, high mixed liquor viscosity hampers turbulence on membrane surface that increases membrane fouling. Due to the increase of fouling resistance, flux can decrease more than expected by the water viscosity. Therefore, temperature correction is meaningful only in a narrow temperature range around the reference point especially when rheological changes of liquid affects membrane performance.

Figure 4-15 shows the fluctuation of TMP and water temperature in the BEMR system. If the range of water temperatures fluctuates widely, temperature correction becomes increasingly inaccurate. For instance, when temperature decreases from 30°C to 5°C in a full scale MBR plant, the sustainable average daily flow declines by 63% (GE Water, 2011) while the correction equation predicts only 48% decline.

4.3 PHASE 3 – TEP

In the last decade, MBR technology has become a competitive technology for advanced treatment and recycling of industrial and municipal wastewater in many regions of the world (Lesjean and Huisjes, 2008). In order to find a solution to one of the biggest hindrances of this technology, membrane fouling studies have multiplied in the recent years. Among these studies, foulant characterization is a major research issue in MBR technology. Some of these studies concluded that extracellular polymeric substances (EPS) in the sludge are involved in the fouling process, nevertheless the relationship between EPS and fouling is not clear yet. The term EPS encompasses a large quantity of compounds of different nature produced by the micro-organisms in the biomass, but in the practice they are monitored as a sum of the polysaccharides (PS) and proteins contained in the sludge. A linear correlation between PS concentration and fouling rate was found (Lesjean et al., 2005), while in other studies this could not be observed (Drews et al., 2007). There is general agreement that PS are one of the major contributors to the membrane fouling process. However, fouling investigations have mainly focused on their concentration, and rarely on their nature. Nevertheless, in order to clarify the importance of EPS in membrane fouling it is necessary to get a better understanding of their properties and composition. In other fields of membrane filtration like wine filtration, the flux decline related to polysaccharides appeared to depend more on the respective amounts of the different polysaccharides than on the total polysaccharide content. Applying this to MBR technology would convert the EPS paradox in a question of quality and not of quantity.

EPS are also relevant in other fields like oceanography or seawater desalination. In these fields, TEP have received increasing attention in the last decade. TEP are very sticky particles that exhibit the characteristics of gels, and consist predominantly of acidic polysaccharides (Passow, 2002). Although TEP analysis was not yet applied to wastewater treatment technology, the relationship between TEP and fouling has been already mentioned. Some authors proposed that TEP in source waters is 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 (Berman and Holenberg, 2005).

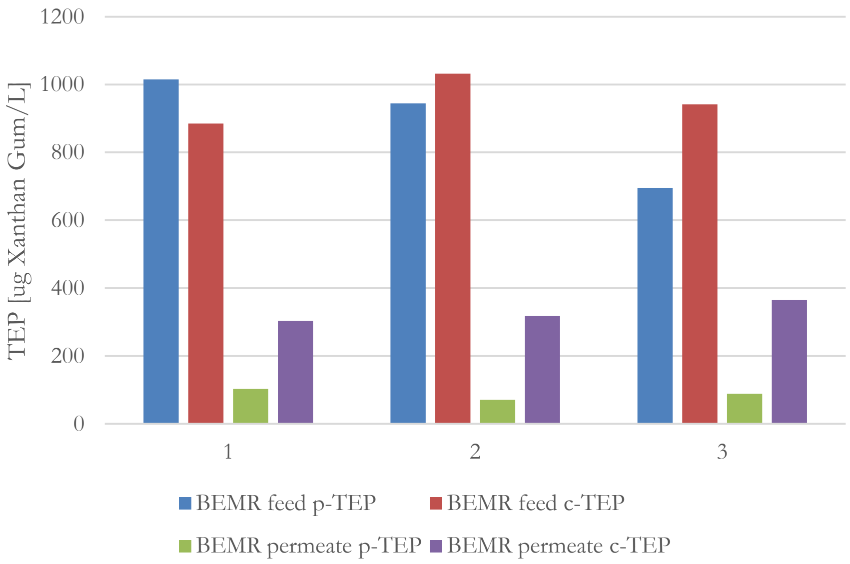

Figure 4-16 - TEP concentrations in the membrane reactor and in its permeate

Figure 4-16 shows typical TEP concentrations in the BEMR that has been operated for six months. As expected, concentrations are significantly lower in the membrane permeate, which means that the UF membrane is effective at retaining this fraction of PS. Generally speaking, the colloidal fraction results to be more abundant than the particulate one, and this is clearly more evident in the permeate, in which the only presence of particulate TEP is due to reaggregation of smaller particles. These results are in line with other studies recently published (Van Nevel et al., 2012).

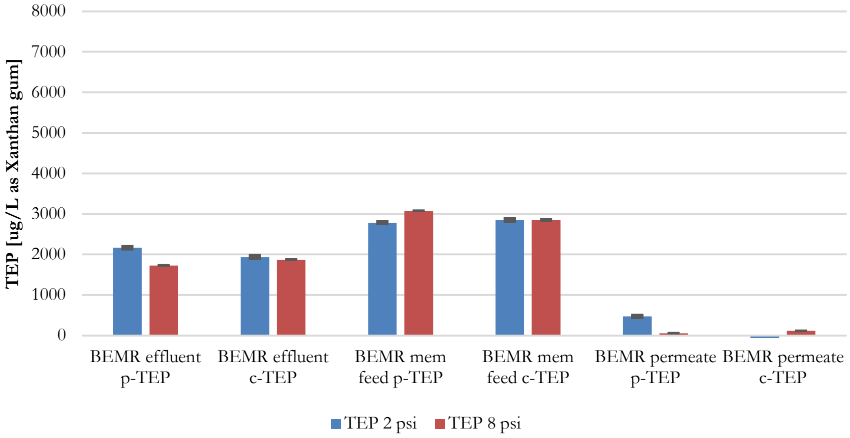

Figure 4-17 - TEP concentrations at 20 LMH at different times and sampling points

Figure 4-17 shows TEP concentrations in the biological effluent, in the membrane reactors and in the permeate, both at the beginning (1 psi) and at the end (8 psi) of the experiment at 20 LMH.

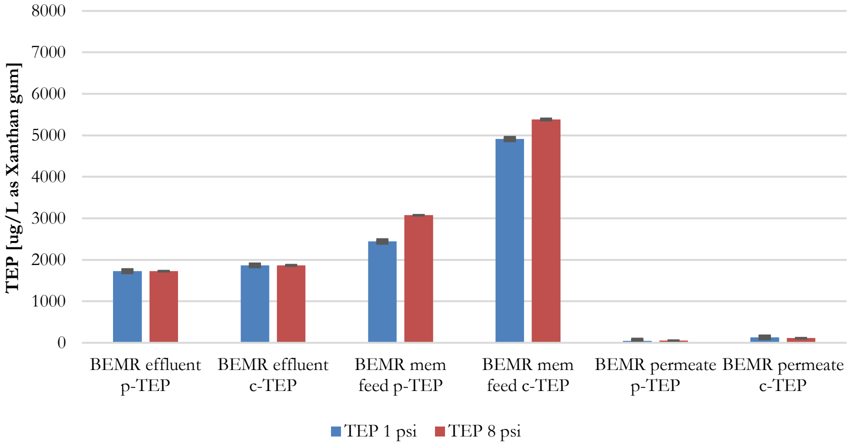

Figure 4-18 - TEP concentrations at 30 LMH at different times and sampling points

Figure 4-18 shows TEP concentrations in the biological effluent, in the membrane reactors and in the permeate, both at the beginning (1 psi) and at the end (8 psi) of the experiment at 30 LMH, in which increasing levels of cTEP in the bulk of the membrane reactor are recorded. This can be regarded as a consequence of reduced HRT and physical barrier offered by the membrane.

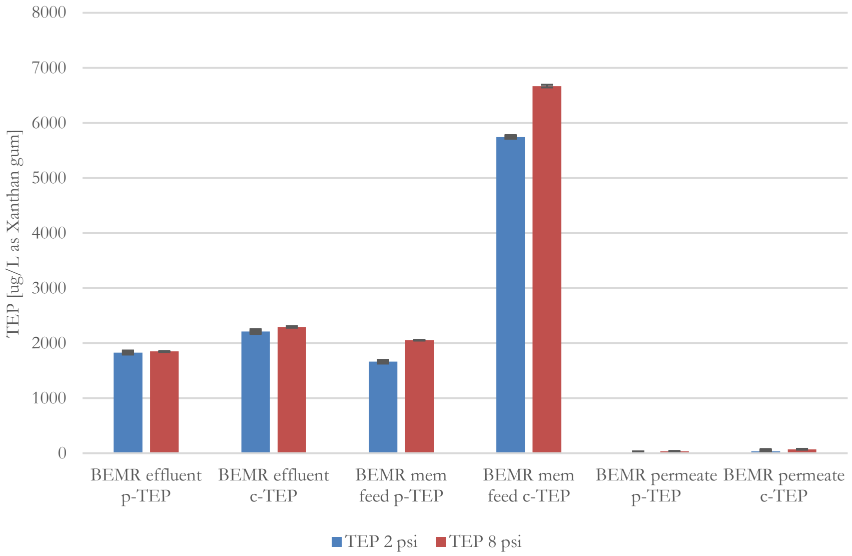

Figure 4-19 - TEP concentrations at 40 LMH at different times and sampling points

Figure 4-19 shows TEP concentrations in the biological effluent, in the membrane reactors and in the permeate, both at the beginning (1 psi) and at the end (8 psi) of the experiment at 40 LMH, in which cTEP in the bulk of the membrane reactor reach a peak. The link between TEP and TMP (and, in turn, membrane fouling) is evident and pseudo-linear.

The results obtained from the first monitoring study of TEP in BEMRs show the significance of this parameter for the research on fouling in MBRs. The relationship of this parameter with the fouling rate has been highlighted after finding a linear correlation between TMP values and TEP concentrations measured for more than six months. Nevertheless, the TEP fraction of the PS is not the only one responsible for fouling.

After chemical cleaning of the membrane, no increment of the concentration of TEP was observed, in contrast to what elsewhere reported for conventional MBRs. The only weak correlation between PS and TEP concentrations demonstrate that the Alcian blue method measures a different fraction of polysaccharides than the conventionally measured one according to Dubois et al. (1956). The occurrence of TEP in permeate and wastewater filtrate was also studied in the BEMR unit investigated.

The Alcian blue method for TEP analysis offers various advantages over the conventional method for PS analysis: it is simple and quicker, the dye is non-toxic and no strong acids are used. Besides, using the method of Dubois et al. (Dubois et al., 1956), the interference of nitrate and nitrite need to be corrected, which provides a further time and cost disadvantage.

5 CONCLUSIONS

It is a well estabilished notion that nowadays MBRs show some relevant edge over CAS treatments in terms of effluent quality, reliability and reclamation issues. Nevertheless, economic constraints still favour conventional biological treatment, especially in developing countries where limited budget do not allow water managers to invest in expensive units. Notwithstanding this aspect, MBRs are steadily spreading worldwide, mainly because of lower installation expenses.

Despite about twenty years of scientific research on the composite topic of fouling in MBRs, many questions still need an answer. On top of that, some recent results tend to be contradicting – mostly because of the well-known disomogeneity among fouling characterisation methods employed by researchers. At present, full-scale MBR plants rely on a range of conventional solutions to deal with the fouling issue, namely physical and chemical procedures. While these solutions effectively help reducing fouling, nothing is done in order to reduce the phenomenon development itself.

Scientists, on the other hand, are extensively focusing on innovative methods to cope with this critical issue. New materials have been developed to enhance filtration (e.g. polymeric membranes) and additives are tested – such as nanomaterials and activated carbon – as flux enhancers.

In addition, the filtration time, the operation constraints(constant flux/constant TMP), and the cleaning protocol are also crucial elements for which experiments are designed.

The critical flux concept and its determination with the flux-stepping experiment remains an interesting tool to assess fouling propensity for a given operating condition, but cannot be used for long-term filtration predictions. Instead, the concept of sustainable flux, for which filtration can be maintained over an extended period of time, is more appropriate for real MBR plants. Effectiveness and strategies for physical and chemical cleanings are underreported in the open literature, and there are still opportunities to match cleaning protocols with the foulant species present.

At present, it is still difficult to propose a solution which could definitely predict and/or model MBR fouling. The large number of studies published on the subject reveals the complex interactions existing between the different fouling parameters. Further understanding of the nature of MBR foulants and their interactions with the membrane material may provide new directions for cleaning agents and protocols, and fouling mitigation strategies for MBRs. In that effort, previous studies reported for flocculation, settling and dewatering of activated sludge can be used as interesting parallels.

In conclusion, although a precise indication cannot be offered, future advances in fouling mitigation for the next decade can be expected expecially from the development of control and additives dosing strategies as well as the manipulation of microbial populations.

Finally, aim of the present study was to develop innovative strategies to control and contrast fouling in MBRs. Each of the three phases implemented represents a step toward membrane fouling control.

5.1 CONCLUSIONS – PHASE 1

In Phase 1, physical barriers have been studied in order to prevent fouling layer compression effect. To this extent, nanomaterials have been developed to provide an effective, non-compressible coating onto the membrane surface.

The presence of a foulant, namely sodium alginate, led to a sharp increase in TMP during filtration tests at constant flux. This compound generates highly compressible fouling layers, and a subsequent increase in resistance once the layer gets compressed. One of the main results of this study is that the fouling layer becomes non-compressible when inert particles are introduced in the reactor, and size of the pores can be kept constant over time.

Notwithstanding the effect due to the presence of particles, this work firstly shows that the formation of a non-compressible cake might be an important effect in the improvement of filtration performances. What is more, the formation of a more structured and engineered fouling layer may limit the fouling compression phenomenon. The achieved reduction in TMP levels limited the frequency of chemical cleanings; addition of nanospheres at a concentration of 200 mg/L, or even lower, can beneficially extend filtration periods. Another finding consists in the dependence of the cake resistance on the diameter and concentration of the nanosphere introduced in the reactor: bigger elements provide larger pores in the cake and therefore attain lower TMP values.

Results show that significant reductions in TMP levels (up to 40% after 3 hours) can be achieved, the greatest enhancement being accomplished with larger nanoparticles, which provided wider channels for the bulk to filtrate.

In addition, higher concentration of inert elements led to a more marked TMP decrease since the engineered layer thickness increases, preventing the foulant agent to deposit onto the membrane surface. Nonetheless, further research is needed in order to test the cake resistance reduction using aeration in the MBR unit, and therefore considering an additional shear stress in the model; subsequently, the system has to be tested during the filtration of a real wastewater. The final step of this project will consist in a full scale application for a sidestream MBR unit. In conclusion, these results show that if the fouling layer structuring is controlled and taken into consideration, the amount of chemical compounds added into an MBR could be strongly reduced.

5.2 CONCLUSIONS – PHASE 2

In Phase 2, a BEMR system has been developed and operated continuously for six months, in order to understand its propensity to develop membrane fouling if compared to a conventional MBR. Among inspected parameters, TEP have been extremely useful to connect foulants' concentrations to TMP levels at different permeate fluxes.

In terms of COD removal efficiency, the BEMR showed almost complete biodegradation of organic matter – feeding the reactor with a synthetic wastewater of 300 mg/L as COD. Residual COD in the biological effluent was due to detached biomass, as sCOD tests showed.

As membrane fouling may differ between the new BEMR and conventional MBRs, we have investigated TMP and their characteristics in membrane fouling of both reactors at various HRTs, and further evaluated membrane cleaning of reactors for comparison. An overall study goal is to reduce membrane fouling commonly encountered in MBRs.

TMP trends at 20, 30 and 40 LMH showed fair reduction of pressure values if compared to a conventional MBR. Although best results were achieved at 20 LMH, even higher permeate fluxes showed significant improvements in terms of performance. Confined biomass helped retain higher concentration of microorganisms and limited presence of biosolids at the bulk-membrane interface, which eventually prevented fouling development.

In the bio-entrapped membrane reactor, TMP arose faster as HRT decreased. The BEMR was less susceptible to fouling, and it sustained a longer service duration than did the conventional MBR.

5.3 CONCLUSIONS – PHASE 3

In Phase 3, TEP development and removal have been studied in the BEMR. The BEMR produced less TEP than conventional MBRs do, due to slow-growing microorganisms with long SRT in the new bioreactor.

Both MBRs produce primarily colloidal TEP, which likely caused membrane pores clogging. In such conditions, slower growing species with the ability to decompose less-biodegradable compounds have the opportunity to proliferate. In other words, in BEMRs/MBRs selection among microorganisms is primarily made by their capability to degrade the substrate, which is also the primary purpose of the treatment process. This, in turn, can lead to extensive colloidal TEP production which seems to cause fouling at high rates.

BEMR appears promising in controlling membrane fouling, requiring less frequent chemical cleaning, and being more economical to operate.
The first attempt to monitor the TEP concentration in a BEMR highlights the potential of this parameter as a fouling indicator for MBR systems. TEP showed the typical behavior of microbial by-products after experiencing a process disturbance, after which the concentration of TEP increased, whereas SMP concentrations in the units stayed stable. TEP monitoring seems to be an additional useful tool for MBR investigation that may help understanding the complex phenomenon of membrane fouling.

REFERENCES

Ahmed, Z., Cho, J., Lim, B.-R., Song, K.-G., Ahn, K.-H., 2007. Effects of sludge retention time on membrane fouling and microbial community structure in a membrane bioreactor, J. Membr. Sci. 287 211–218.

Al-Halbouni, D., Traber, J., Lyko, S., Wintgens, T., Melin, T., Tacke, D., Janot, A., Dott, W., Hollender, J., 2008. Correlation of EPS content in activated sludge at different sludge retention times with membrane fouling phenomena, Water Res. 42 1475–1488.

Alldredge, A.L., Passow, U., Logan, B.E., 1993. The abundance and significance of a class of large, transparent organic particles in the ocean, Deep Sea Res. Part I: Oceanogr. Res. Papers 40 (6) 1131–1140.

Al-Malack, M.H., 2006. Determination of biokinetic coefficients of an immersed membrane bioreactor, J. Membr. Sci. 271, 47-58.

Ang, W.S., Lee, S., Elimelech, M., 2006. Chemical physical aspects of cleaning organic-fouled reverse osmosis membranes. Journal of Membrane Science 272, 198–210.

Arabi, S., Nakhla, G., 2008. Impact of protein/carbohydrate ratio in the feed wastewater on the membrane fouling in membrane bioreactors, J. Membr. Sci. 324 142–150.

Arevalo, J., Garralon, G., Plaza, F., Moreno, B., Perez, J., Gomez, M.A., 2009. Wastewater reuse after treatment by tertiary ultrafiltration and a membrane bioreactor (MBR): a comparative study. Desalination 243 32-41.

Arruda, S.H.S., Henriques, A.A., Fatibello-Filho, O.F., 2004. A rapid spectrophotometric method for the determination of transparent expolymer particles (TEP) in freshwater, Talanta 62 81–85.

Artiga, P., Oyanedel, V., Garrido, J.M., Mendez, R., 2005. An innovative biofilm-suspended biomass hybrid membrane bioreactor for wastewater treatment. Desalination 179 (1-3), 171-179.

Bacchin, P., Aimar, P., Field, R.W., 2006. Critical and sustainable fluxes: theory, experiments and applications, J. Membr. Sci. 281 42–69.

Barceló, D., Radjenović, J., Matošić, M., Mijatović, I., Petrović, M.,. 2008. Membrane bioreactor (MBR) as an advanced wastewater treatment technology. In D. Barceló, & M. Petrović (Eds.), Emerging contaminants from industrial and municipal waste. Springer Berlin / Heidelberg.

Barker P.S., Dold P.L., 1996. Sludge production and oxygen demand in nutrient removal activated sludge system, Water Sci. Technol. 34, 43-50.

Barker, D.J., Stuckey, D.C., 1999. A review of soluble microbial products (SMP) in wastewater treatment systems. Water Research 33 (14), 3063-3082.

Bar-Zeev, E., Berman-Frank, I., Liberman, B., Rahav, E., Passow, U., Berman, T., 2009. Transparent exopolymer particles: potential agents for organic fouling and biofilm formation in desalination and water treatment plants. Desalination and Water Treatment 3, 136-142.

Belfort G., Davis R.H., Zydney A.L., 1994. Review-The behavior of suspensions and macromolecular solutions in crossflow microfiltration, J. Membr. Sci. 96, 1-58.

Berman, T., Holenberg, M., 2005. Don't fall foul of biofilm through high TEP levels, Filtr. Sep. 42 (4) 30–32.

Berman, T., Mizrahi, R., Dosoretz, C.G., 2011. Transparent exopolymer particles (TEP): a critical factor in aquatic biofilm initiation and fouling on filtration membranes. Desalination 276, 184-190.

Berman, T., Parparova, R., 2010. Visualization of transparent exopolymer particles (TEP) in various source waters. Desalination and Water Treatment 21, 382-389.

Bérubé P.R., G. Afonso, F. Taghipour, C.C.V. Chan, 2006. Quantifying the shear at the surface of submerged hollow fiber membranes, J. Membr. Sci. 279 495–505.

Bessiere Y., N. Abidine, P. Bacchin, 2005. Low fouling conditions in dead-end filtration: evidence for a critical filtered volume and interpretation using critical osmotic pressure, J. Membr. Sci. 264 37–47.

Bessiere, Y., Abidine, N., Bacchin, P., 2005. Low fouling conditions in dead-end filtration: evidence for a critical filtered volume and interpretation using critical osmotic pressure, J. Membr. Sci. 264 37–47.

Beun, J.J., Heijnen, J.J., Van Loosdrecht, M.C.M., 2001. N-removal in a granular sludge sequencing batch airlift reactor, Biotechnol Bioeng 75, 82-92.

Bolton G., LaCasse D., Kuriyel R. (2006). Combined models of membrane fouling: development and application to microfiltration and ultrafiltration of biological fluids, J. Membr. Sci., 277, 75–84.

Bouhabila, E.H., Ben Aim, R., Buisson, H., 2001. Fouling characterisation in membrane bioreactors, Sep. Purif. Technol. 22–23 123–132.

Bowen W.R., Calvo J.I., Hernandez A. (1995). Steps of membrane blocking in flux decline during protein microfiltration, J. Membr. Sci. 101, 153–165.

Bracklow, U., Carvalho, G., Drews, A., Pallasch, M., Barjenbruch, M., Kraume, M., 2008. Performance and bacteria population of a laboratory scale MBR, in: Book of Abstracts of SIDISA08, Florence, p. 101.

Bradford, M., 1974. A rapid and sensitive method for the quantification of microgram quantities of protein utilizing the principle of protein–dye binding, Anal. Chem. 72 248–254.

Brauns, E., 2003. Could fuzzy logic be the key to membrane fouling control? Desal. Water Reuse 13 18–24.

Brauns, E., Teunckens, D., Dotremont, C., van Hoof, E., Doyen, W., Vanhencke, D., 2005. Dead-end filtration experiments on model dispersions: comparison of VFM data and the Kozeny–Carman model, Desalination 177 303–315.

Brepols, C., Drensla, K., Janot, A., Trimborn, M., Engelhardt, N., 2008. Strategies for chemical cleaning in large scale membrane bioreactors, Water Sci. Technol. 57 457–463.

Broeckmann, A., J. Busch, T. Wintgens, W. Marquardt, 2006. Modeling of pore blocking and cake layer formation in membrane filtration for wastewater treatment, Desalination 189 97–109.

Busch, J., Cruse, A., Marquardt, W., 2007. Modeling submerged hollow-fiber membrane filtration for wastewater treatment, J. Membr. Sci. 288 94–111.

Canales, A., Pareilleux, A., Rols, J.L., Goma, G., Huyard, A., 1994. Decreased sludge production strategy for domestic wastewater treatment, Water Sci Technol 30, 97–106.

Chae S.R., S. Wang, Z.D. Hendren, M.R. Wiesner, Y. Watanabe, C.K. Gunsch, 2009. Effects of fullerene nanoparticles on Escherichia coli K12 respiratory activity in aqueous suspension and potential use for membrane biofouling control, J. Membr. Sci. 329 68–74.

Chaize, S., Huyard, A., 1991. Membrane bioreactor on domestic wastewater treatment: sludge production and modelling approach, Water Sci. Tech. 23, 1591–1600.

Chang I.S., Kim S.N. (2005). Wastewater treatment using membrane filtration-effect of biosolids concentration on cake resistance, Proc. Biochem. 40, 1307–1314.

Chang, I.-S., Le-Clech, P., Jefferson, B., Judd, S., 2002. Membrane fouling in membrane bioreactors for wastewater treatment, Environ. Eng. Sci. 128 (11) 1018–1029.

Chang, I.S., Lee, C.H., 1998. Membrane filtration characteristics in membrane coupled activated sludge system - the effect of physiological states of activated sludge on membrane fouling, Desalination. 120, 221-233.

Charlery, C., Drews, A., Kraume, M., Kroh, L.W., 2009. Advanced analysis of polysaccharides in MBR fouling by chromatography, in: Book of Proceedings of the Final MBR-Network Workshop, Berlin, pp. 103–104.

Chen G.H., Yip W.K., Mo H.K., Liu Y., 2001. Effect of sludge fasting/ feasting on growth of activated sludge cultures, Water Res. 35, 1029–1037.

Chiemchaisri C., Wong Y.K., Urase T., Yamamoto K., 1993. Organic stabilisation and nitrogen removal in a membrane separation bioreactor for domestic wastewater treatment, Filtr Sep 30, 247-252.

Chisti, M.Y., B. Halard, M. Moo-Young, 1988. Liquid circulation in airlift reactors, Chem. Eng. Sci. 43 (3) 451–457.

Cho, B.D., Fane, A.G., 2002. Fouling transients in nominally subcritical flux operation of a membrane bioreactor. Journal of Membrane Science 209 (2), 391-403.

Cho, J., Song, K.G., Lee, S.H., Anh, K.H., 2005. Sequencing anoxic/ anaerobic membrane bioreactor (SAM) pilot plant for advanced wastewater treatment. Desalination 178 (1-3), 219-225.

Choi, E., Eum, Y., Gil, K.I., Oa, S.W., 2004. High strength nitrogen removal from nightsoil and piggery wastes, Water Sci Technol 49(5-6), 97-104.

Choi, J.G., Bae, T.H., Kirn, J.H., Tak, T.M., Randall, A.A., 2002. The Behavior of Membrane Fouling Initiation on the Crossflow Membrane Bioreactor System, J. Membr. Sci. 203, 103.

Chudacek, M.W., Fane, A.G., 1984. The dynamics and polarisation in unstirred and stirred ultrafiltration, J. Membr. Sci. 21 145–160.

Chung, J., Kim, Y., Lee, D.J., Shim, H., Kim, J.O., 2006. Characteristics of denitrifying phosphate accumulating organisms in an anaerobic-intermittently aerobic process, J Environ Eng Sci 23(6), 977-989.

Cicek N., Macomber J., Davel J., Suidan M. T., Audic J., Genestet P., 2001. Effect of solids retention time on the performance and biological characteristics of a membrane bioreactor. Water Sci Technol 43, 43.

Cirja, M., Ivashechkin, P., Schäffer, A., Corvini, F. X., 2008. Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR).

Clara, M., Kreuzinger, N., Strenn, B., Gans, O., & Kroiss, H., 2005. The solids retention time—a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. Water Research, 39(1), 97-106.

Cote, P., Buisson, H., Praderie, M., 1998. Immersed membranes activated sludge process applied to the treatment of municipal wastewater. Water Science and Technology 38, 437.

Cote, P., Buisson, H., Pound, C., Arakaki, G., 1997. Immersed membrane activated sludge for the reuse of municipal wastewater, Desalination 113, 189.

Cui, Z.F., S. Chang, A.G. Fane, 2003. The use of gas bubbling to enhance membrane processes, J. Membr. Sci. 221 1–35.

De la Torre, T., Iversen, V., Meng, F., Stüber, J., Drews, A., Lesjean, B., Kraume, M., 2010. Searching for a universal fouling indicator for MBR, Desalination Water Treatm. 18 264–269.

De la Torre, T., Iversen, V., Moreau, A., Stüber, J., 2009. Filtration charaterization methods in MBR systems: a practical comparison, Desalination Water Treatm. 9 15–21.

De la Torre, T., Lesjean, B., Kraume, M., Drews, A., 2008. Monitoring of transparent exopolymer particles (TEP) in a membrane bioreactor (MBR) and correlation with other fouling indicators, Water Sci. Technol. 58 1903–1909.

Delgado S., R. Villarroel, E. González, 2008. Effect of the shear intensity on fouling in a submerged membrane bioreactor for wastewater treatment, J. Membr. Sci. 311 173–181.

Di Trapani D., Capodici M., Cosenza A., Di Bella G., Mannina G., Torregrossa M., Viviani G. (2011). Evaluation of biomass activity and wastewater characterization in a UCT-MBR pilot plant by means of respirometric techniques, Desalination 269, 190-197.

Dong, B., Jiang, S., 2009. Characteristics and behaviors of soluble microbial products in sequencing membrane bioreactors at various sludge retention times, Desalination 243 240–250.

Drews, A., 2010. Membrane fouling in membrane bioreactors-Characterisation, contradictions, cause and cures. Journal of Membrane Science 363, 1-28.

Drews, A., Arellano-Garcia, H., Schöneberger, J., Schaller, J., Wozny, G., Kraume, M., 2009. Model-based recognition of fouling mechanisms in membrane bioreactors, Desalination 236 224–233.

Drews, A., Kraume, M., 2005. Process improvement by application of membrane bioreactors, Trans. IChemE A3, Chem. Eng. Res. Des. 83 276–284.

Drews, A., Lee, C.-H., Kraume, M., 2006. Membrane fouling—a review on the role of EPS, Desalination 200 186–188.

Drews, A., Mante, J., Iversen, V., Vocks, M., Lesjean, B., Kraume, M., 2007. Impact of ambient conditions on SMP elimination and rejection in MBR, Water Res. 41 3850–3858.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances, Anal. Chem. 28 350–356.

Ducom, G., F.P. Puech, C. Cabassud, 2002. Air sparging with flat sheet nanofiltration: a link between wall shear stresses and flux enhancement, Desalination 145 97–102.

Eckenfelder W., Grau P. (1998). Activated sludge process design and control: Thery and practice (2nd ed.), Lancaster, PA: Technomic.

Eckstein E.C., Bailey D.G., Shapiro A.H., 1977. Self-diffusion of particles in shear flow of a suspension, J. Fluid Mech. 79 191-208.

Elmaleh, S., Ghaffor, N., 1996. Cross-flow ultrafiltration by hydrocarbon and biological solid mixed suspensions, J. Membr. Sci. 118 111–120.

EPA, 1989. EPA/ASCE design manual on fine pore aeration. Cincinnati, Ohio: EPA.

Ernst, M., Mehrez, R., Drews, A., Iversen, V., Kraume, M., Jekel, M., 2007. Continuous measurement and control of fouling active compounds in membrane bioreactor systems, Water Sci. Technol. 56 (7) 11–19.

Essemiani, K., G. Ducom, C. Cabassud, A. Liné, 2001. Spherical cap bubbles in a flat sheet nanofiltration module: experiments and numerical simulation, Chem. Eng. Sci. 56 6321–6327.

Evenblij H., S. Geilvoet, J.H.J.M. van der Graaf, H.F. van der Roest, 2005. Filtration characterization for assessing MBR performance: three cases compared, Desalination 178 115–124.

Fabrega, J., Renshaw, J.C., Lead, J.R., 2009. Interactions of silver nanoparticles with Pseudomonas putida biofilms. Environmental Science and Technology 43 (23), 9004-9009.

Fan X.J., Urbain V., Qian Y., Manem J. (1996). Nitrification and mass balance with a membrane bioreactor for municipal wastewater treatment, Water Sci Technol 34, 129-136.

Fane A.G., A. Yeo, A. Law, K. Parameshwaran, F. Wicaksana, V. Chen, 2005. Low pressure membrane processes—doing more with less energy, Desalination 185 159–165.

Fane, A.G., 2005. Submerged membrane processes—factors affecting performance in hybrid systems & MBRs, in: AWA Specialty Conference—Membranes & Desalination, Adelaide, February 23–25, 2005.

Fane, A.G., 2009. MBRs and the TMP jump—self accelerating fouling phenomena, in: Book of Proceedings of the Final MBR-Network Workshop, Berlin, 2009, pp. 5–6.

Fang, H.H., Shi, X., Zhang, T., 2006. Effect of activated carbon on fouling of activated sludge filtration. Desalination 189, 193-199.

Ferrando, M., Rozek, A., Zator, M., López, F., Güell, C., 2005. An approach to membrane fouling characterization by confocal scanning laser microscopy, J. Membr. Sci. 250 283–293.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling, J. Membr. Sci. 100 259–272.

Flemming, H.C., Wingender, J., 2001. Relevance of microbial extracellular polymeric substances (EPSs). Part I. Structural and ecological aspects. Water Science and Technology 43 (6), 1-8.

Foley G., P.F. MacLoughlin, D.M. Malone, 1992. Preferential deposition of smaller cells during cross-flow microfiltration of a yeast suspension, Biotechnol. Technol. 6 (2) 115–120.

Frank B.P., Belfort G. (2003). Polysaccharides and sticky membrane surfaces: critical ionic effects, J. Membr. Sci. 212, 205–212.

Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin, Water Res. 30 1749–1758.

Galinha, C.F., Portugal, C., Carvalho, G., Crespo, J.G., Reis, M.A.M., 2007. Fluorescence spectroscopy as a tool for performance monitoring of membrane bioreactors in wastewater treatment systems, in: Membrane Technologies for Wastewater Treatment and Reuse (7), Proceedings of the 2nd IWA Nat. Young Water Professionals Conference, Berlin, pp. 45–50.

Gander M.A., Jefferson B., Judd S.J. (2000). Membrane bioreactors for use in small wastewater treatment plants: membrane materials and effluent quality, Water Sci. Technol. 41, 205–211.

Gao M., Yang M., Li H., Wang Y., Pan F., 2004. Nitrification and sludge characteristics in a submerged membrane bioreactor on synthetic inorganic wastewater, Desalination 170, 177-185.

Geilvoet, S., Van der Graaf, J., Van Nieuwenhuijzen, A., 2008. MBR activated sludge filterability alteration in stress circumstances, in: ICOM 2008, Honolulu, July 12–18, 2008.

Geilvoet, S.P., Remy, M., Evenblij, H., Temmink, H., van der Graaf, J.H.J.M., 2006. Tracing membrane foulants in membrane bioreactors by filtration characterization and fractionation, Water Sci. Technol.: Water Supply 6 (1) 165–172.

Geissler, S., Wintgens, T., Melin, T., Vossenkaul, K., Kullmann, C., 2005. Modelling approaches for filtration processes with novel submerged capillary modules in membrane bioreactors for wastewater treatment, Desalination 178 125–134.

Germain E., Stephenson T., Pearce P. (2005). Biomass characteristics and membrane aeration: toward a better understanding of membranefouling in submerged membrane bioreactors (MBRs), Biotechnol Bioeng 90, 316–322.

Göbel, A., McArdell, C. S., Joss, A., Siegrist, H., & Giger, W., 2007. Fate of sulfonamides, macrolides, and trimethoprim in different wastewater treatment technologies. Science of the Total Environment, 372(2–3), 361-371.

Grace H. P. (1956). Structure and performance of filter media, AIChE J. 2, 307.

Green G., Belfort G., 1980. Fouling of ultrafiltration membranes: Lateral migration and the particle trajectory model, Desalination 35, 129-147.

Grelier, P., Rosenberger, S., Tazi-Pain, A., 2006. Influence of sludge retention time on membrane bioreactor hydraulic performance, Desalination 192 (1–3) 10–17.

Guglielmi, G., Saroj, D.P., Chiarani, D., Andreottola, G., 2007. Sub-critical fouling in a membrane bioreactor for municipal wastewater treatment:

experimental investigation and mathematical modelling, Water Res. 41 3903–3914.

Gujer W., Henze M., Mino T., van Loosdrecht M., 1999. Activated sludge model, Water Sci. Technol. 39, 183-193.

Guo, W.S., Vigneswaran, S., Ngo, H.H., Van Nguyen, T.B., Ben Aim, R., 2006. Influence of bioreactor on a long term operation of a submerged membrane adsorption hybrid system. Desalination 191, 92-99.

Haberkamp, J., Ruhl, A.S., Ernst, M., Jekel, M., 2007. Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behavior in ultrafiltration, Water Res. 41 3794–3802.

Hai F.I., K. Yamamoto, K. Fukushi, F. Nakajima, 2011. Fouling resistant compact hollow-fiber module with spacer for submerged membrane bioreactor treating high strength industrial wastewater, J. Membr. Sci. 317 34–42.

Hanft, S., 2006. Membrane Bioreactors in the Changing World Water Market. In: Business Communications Company Inc. Report C-240.

Hardt F.W., Clesceri L.S., Nemerow N.L., Washington D.R. (1970). Solid separation by ultrafiltration for concentrated activated sludge, J Water Pollut Control Fed 42, 2135.

Harmant, P., Aimar, P., 1996. Coagulation of colloids retained by porous wall, AIChE J. 42 3523–3532.

Harscoat C., Jaffrin M.Y., Bouzerar R., Courtois J., 1999. Influence of fermentation conditions and microfiltration processes on membrane fouling during recovery of glucuronane polysaccharides from fermentation broths, Biotechnol. Bioeng. 65, 500–511.

Hermia, J., 1982. Constant pressure blocking laws—application to power-law non-Newtonian fluids, Trans. IChemE 60 183–187.

Hlavacek, M., Bouchet, F., 1993. Constant flowrate blocking laws and an example of the application to dead-end microfiltration of protein solutions, J. Membr. Sci. 82 285–295.

Horan, N., 1990. Biological Wastewater Treatment Systems: Theory and Operation. Wiley, Chichester.

Huang X., Gui P., Qian Y. (2001). Effect of sludge retention time on microbial behaviour in a submerged membrane bioreactor, Process Biochem. 36, 1001-1006.

Hughes, D.J., Cui, Z.F., Field, R.W., Tirlapur, U.K., 2007. Membrane fouling by cell–protein mixtures: in situ characterisation using multi-photon microscopy, Biotechnol. Bioeng. 96 (6) 1083–1091.

Huyskens, C., Brauns, E., Van Hoof, E., De Wever, H., 2008. A new method for the evaluation of the reversible and irreversible fouling propensity of MBR mixed liquor, J. Membr. Sci. 323 185–192.

Hwang, B.-K., Lee, W.-N., Yeon, K.-M., Park, P.-K., Lee, C.-H., Chang, I.-S., Drews, A., Kraume, M., 2008. Correlating TMP increases with microbial characteristics in the bio-cake on the membrane surface in a membrane bioreactor, Environ. Sci. Technol. 42 3963–3968.

Ivanonic, I., Leiknes, T., Ødegaard, H., 2006. Influence of loading rates on production on characteristics of retentate from a biofilm membrane bioreactor (BF-MBR). Desalination 199 (1-3), 490-492.

Iversen, V., H. Koseoglu, N.O. Yigit, A. Drews, M. Kitis, B. Lesjean, M. Kraume, 2009. Impact of membrane flux enhancers on respiration and nutrient removal in MBRs, Water Res. 43 822–830.

Iversen V., J. Mohaupt, A. Drews, B. Lesjean, M. Kraume, 2008. Side effects of the flux enhancing in membrane bioreactors, Water Sci. Technol. 57 (1) 117–123.

Jarusutthirak, C., G. Amy, J.P. Croué, 2002. Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes, Desalination 145 247–255.

Jarusutthirak, C., Amy, G., 2006. Role of soluble microbial products (SMP) in membrane fouling and flux decline. Environmental Science and Technology 40 (3), 969-974.

Jiang, T., Kennedy, M.D., van der Meer, W.G.J., Vanrolleghem, P.A., Schippers, J.C., 2003. The role of blocking and cake filtration in MBR fouling, Desalination 157 335–434.

Jiang, T., Myngheer, S., De Pauw, D.J.W., Spanjers, H., Nopens, I., Kennedy, M.D., Amy, G., Vanrolleghem, P.A., 2008. Modelling the production and degradation of soluble microbial products (SMP) in membrane bioreactors (MBR), Water Res. 42 4955–4964.

Jofre J., Olle E., Ribas F., Vidal A., Lucena F., 1995. Potential usefulness of bacteriophages that infect Bacteroides fragilis as model organisms for monitoring virus removal in drinking water treatment plants, Appl Environ Microbiol 61, 3227-3231.

Jons, S., Ries, P., McDonald, C.J., 1999. Porous latex composite membranes: fabrication and properties. Journal of Membrane Science 155 (1), 79-99.

Joss, A., Böhler, M., Wedi, D., Siegrist, H., 2009. Proposing a method for online permeability monitoring in membrane bioreactors, Water Sci. Technol. 60 497–506.

Judd S.J. (2006) The MBR Book. Elsevier, Oxford, UK.

Judd S.J. (2010) The MBR Book (Second edition). Elsevier, Oxford, UK.

Judd S.J., The status of membrane bioreactor technology, Trends Biotechnol. 26 (2) (2007) 109–116.

Kang, C.W., J. Hua, J. Lou, W. Liu, E. Jordan, 2008. Bridging the gap between membrane bio-reactor (MBR) pilot and plant studies, J. Membr. Sci. 325 861–871.

Kennedy, M.D., Tobar, F.P.M., Amy, G., Schippers, J.C., 2009. Transparent exopolymer particle (TEP) fouling of ultrafiltration membrane systems. Desalination and Water Treatment 6, 169-176.

Kim, J., Deng, Q., Benjamin, M.M., 2008. Simultaneous removal of phosphorus and foulants in a hybrid coagulation/membrane filtration system. Water Research 42, 2017-2024.

Kim, M., Nakhla, G., 2009. Comparative studies on membrane fouling between two membrane-based biological nutrient removal systems, J. Membr. Sci. 331 91–99.

Kim, M.G., Nakhla, G., 2010. Membrane fouling propensity of denitrifying organisms, J. Membr. Sci. 348 197–203.

Kimura K., T. Miyoshi, T. Naruse, N. Yamato, R. Ogyu, Y. Watanabe, 2008. The difference in characteristics of foulants in submerged MBRs caused by the difference in the membrane flux, Desalination 231 268–275.

Kimura, K., Naruse, T., Watanabe, Y., 2009. Changes in characteristics of soluble microbial products in membrane bioreactors associated with different solid retention times: relation to membrane fouling, Water Res. 43 1033–1039.

Knoblock, M.D., Sutton, P.M., Mishra, P.N., Gupta, K., Janson, A., 1994. Membrane biological reactor system for treatment of oily wastewaters. Water Environ Res 66, 133-139.

Koivunen, J., Siitonen, A., Heinonen-Tanski, H., 2003. Elimination of enteric bacteria in biologicalechemical wastewater treatment and tertiary filtration units. Water Res 37 (3), 690-698.

Koseoglu, H., N.O. Yigit, V. Iversen, A. Drews, M. Kitis, M. Kraume, 2008. Effects of several different flux enhancing chemicals on filterability and fouling reduction of membrane bioreactor (MBR) mixed liquors, J. Membr. Sci. 320 57–64.

Kraume M., Bracklow U., Vocks M., Drews A., 2005. Nutrients removal in MBRs for municipal wastewater treatment, Water Sci. Technol 51, 391-402.

Kraume M., D. Wedi, J. Schaller, V. Iversen, A. Drews, 2009. Fouling in MBR—what use are lab investigations for full scale operation? Desalination 236 94–103.

Kromkamp J., F. Faber, C.G.P.H. Schroën, R.M. Boom, 2006. Effects of particle size segregation on crossflow microfiltration performance: control mechanism for concentration polarisation and particle fractionation, J. Membr. Sci. 268 189–197.

Kuhn, R., Pollice, A., Laera, G., Palese, L.L., Lippolis, R., Papa, S., 2007. Standard assays and metaproteomics as new approaches for functional chracterization of membrane bioreactor biomass, in: Membrane

Technologies for Wastewater Treatment and Reuse (7), Proceedings of the 2nd IWA Nat. Young Water Professionals Conference, Berlin, pp. 59–64.

Larsen, P., Nielsen, J.L., Svendsen, T.C., Nielsen, P.H., 2008. Adhesion characteristics of nitrifying bacteria in activated sludge, Water Res. 42 2814–2826.

Laspidou, C.S., Rittmann, B.E., 2002. A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass, Water Res. 36 2711–2720.

Le-Clech, P., 2007. Fouling index for MBR, in: Proceedings of the IWA Workshop Membrane and Fouling Characterisation, Sydney, November 5, 2007.

Le-Clech, P., B. Jefferson, S.J. Judd, 2003. Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor, J. Membr. Sci. 218 117–129.

Le-Clech, P., Chen, V., Fane, A.G., 2006. Fouling in membrane bioreactors used in wastewater treatment. Journal of Membrane Science 284, 17-53.

Lee W.N., W.-S. Cheong, K.-M. Yeon, B.-K. Hwang, C.-H. Lee, 2009. Correlation between local TMP distribution and bio-cake porosity on the membrane in a submerged MBR, J. Membr. Sci. 332 50–55.

Lee, S., Ang, W.S., Elimelech, M., 2006. Fouling of reverse osmosis membranes by hydrophilic organic matter: implications of water reuse. Desalination 187, 313–321.

Lee, W.-N., Chang, I.-S., Hwang, B.-K., Park, P.-K., Lee, C.-H., Huang, X., 2007. Changes in biofilm architecture with addition of membrane fouling reducer in a membrane bioreactor, Process. Biochem. 42 (4) 655–661.

Leiknes, T., H. Bolt, M. Engmann, H. Ødegaard, 2006. Assessment of membrane reactor design in the performance of a hybrid biofilm membrane bioreactor (BF-MBR), Desalination 199 328–330.

Leiknes, T., Ødegaard, H., 2007. The development of biofilm membrane bioreactor. Desalination 202 (1-3), 135-143.

Lesage, N., Sperandio, M., Cabassud, C., 2005. Performances of a hybrid adsorption/submerged membrane biological process for toxic waste removal. Water Science and Technology 51, 173-180.

Lesjean, B., Gnirss, R., Adam, C., Kraume, M., Luck, F., 2003. Enhanced biological phosphorus removal process implemented in membrane bioreactors to improve phosphorus recovery and recycling, Water Sci. Technol, 48, 87-94.

Lesjean, B., Huisjes, E.H., 2008. Survey of the European MBR market: trends and perspectives, Desalination 231 71–81.

Lesjean, B., Rosenberger, S., Laabs, C., Jekel, M., Gnirss, R., Amy, G., 2005. Correlation between membrane fouling and soluble/colloidal organic substances in membrane bioreactors for municipal wastewater treatment. Water Science and Technology 51, 1-8.

Lesjean, B., Rosenberger, S., Laabs, C., Jekel, M., Gnirss, R., Amy, G., 2004. Correlation between membrane fouling and soluble/colloidal organic substances in membrane bioreactors for municipal wastewater treatment, in: WEMT 2004, Seoul, 2004, pp. 525–532.

Li H., A.G. Fane, H.G.L. Coster, S. Vigneswaran, 1998. Direct observation of particle deposition on the membrane surface during crossflow microfiltration, J. Membr. Sci. 149 83–97.

Li, H., Yang, M., Zhang, Y., Yu, T., Kamagata, Y., 2006. Nitrification performance and microbial community dynamics in a submerged membrane bioreactor with complete sludge retention, J. Biotechnol. 123, 60–70.

Li, H., Fane, A.G., Coster, H.G.L., Vigneswaran, S., 1998. Direct observation of particle deposition on the membrane surface during crossflow microfiltration, J. Membr. Sci. 149 83–97.

Li, J., Yang, F., Li, Y., Wong, F.-S., Chua, H.C., 2008. Impact of biological constituents and properties of activated sludge on membrane fouling in a novel submerged membrane bioreactor, Desalination 225 356–365.

Liang, S., Y. Zhao, C. Liu, L. Song, 2008. Effect of solution chemistry on the fouling potential of dissolved organic matter in membrane bioreactor systems, J. Membr. Sci. 310 503–511.

Liang, S., Lui, C., Song, L., 2007. Soluble microbial products in membrane bioreactor operation: behaviors, characteristics, and fouling potential. Water Research 41 (1), 95-101.

Lim, B.S., Choi, B.C., Yu, S.W., Lee, C.G., 2007. Effects of Operational Parameters on Aeration On/Off Time in an Intermittent Aeration Membrane Bioreactor, Desalination 202, 77–82.

Lim, A.L., Bai, R., 2003. Membrane fouling and cleaning in microfiltration of activated sludge wastewater, J. Membr. Sci. 216, 279–290.

Loh, S.T., Beuscher, U., Poddar, T.K., Porter, A.G., Wingard, J.M., Husson, S.M., Wickramasinghe, S.R., 2009. Interplay among membrane properties, protein properties and operating conditions on protein fouling during normal-flow microfiltration, J. Membr. Sci. 332 93–103.

Lousada-Ferreira, M., Geilvoet, S., Moreau, A., Atasoy, E., Krzeminski, P., van Nieuwenhuijzen, A., van der Graaf, J., 2009. MLSS concentration: still a poorly understood parameter in MBR filterability, Desalination 250 6128–6622.

Low, E.W., Chase, H.A., 1999. The effect of maintenance energy requirements on biomass production during wastewater treatment, Water Res 33, 847-853.

Lowry, O., Rosebrough, N., Farr, A., Randall, R., 1951. Protein measurement with the folin phenol reagent, J. Biol. Chem. 193 265–275.

Lu, S.G., Imai, T., Ukita, M., Sekine, M., Higuchi, T., Fukagawa, M., 2001. A model for membrane bioreactor process based on the concept of formation and degradation of soluble microbial products, Water Res. 35 2038–2048.

Lubbecke, S., Vogelpohl, A., Dewjanin, W., 1995. Wastewater treatment in a biological high-performance system with high biomass concentration, Water Res 29, 793-802.

Lyko, S., Al-Halbouni, D., Wintgens, T., Janot, A., Hollender, J., Dott, W., Melin, T., 2007. Polymeric compounds in activated sludge supernatant—characterisation and retention mechanisms at a full-scale municipal membrane bioreactor, Water Res. 41 3894–3902.

Lyko, S., Wintgens, T., Al-Halbouni, D., Baumgarten, S., Tacke, D., Drensla, K., Janot, A., Dott, W., Pinnekamp, J., Melin, T., 2008. Long-term monitoring of a full-scale municipal membrane bioreactor—characterisation of foulants and operational performance, J. Membr. Sci. 317 78–87.

Macomber, J., Cicek, N., Suidan, M.T., Davel, J., Ginestet, P., Audic, J.M., 2005. Biological kinetic data evaluation of an activated sludge system coupled with an ultrafiltration membrane. J Environ Eng 131(4), 579-586.

Malamis, S., Andreadakis, A., 2009. Fractionation of proteins and carbohydrates of extracellular polymeric substances in a membrane bioreactor system. Bioresource Technology 100 (13), 3350-3357.

Marti, E., Monclus, H., Jofre, J., Rodriguez-Roda, I., Comas, J., Balcazar, J.L., 2011. Removal of microbial indicators from municipal wastewater by a membrane bioreactor (MBR). Bioresource Technol. 102 5004-5009.

Masse, A., Sperandio, M., Cabassud, C., 2006. Comparison of sludge characteristics and performance of a submerged membrane bioreactor and an activated sludge process at high solids retention time, Water Res 40, 2405 – 2415.

McAdam E., S.J. Judd, R. Gildemeister, A. Drews, M. Kraume, 2005. Critical analysis of submerged membrane sequencing batch reactor operating conditions, Water Res. 39 4011–4019.

McGahey, C., Olivieri, V.P., 1993. Mechanisms of viral capture by microfiltration, Water Sci Technol 27, 307-310.

Mehrez R., M. Ernst, M. Jekel, 2007. Development of a continuous protein and polysaccharide measurement method by Sequential Injection Analysis for application in membrane bioreactor systems, Water Sci. Technol. 56 (6) 163–171.

Meng, F., Drews, A., Mehrez, R., Iversen, V., Ernst, M., Yang, F., Jekel, M., Kraume, M., 2009. Occurrence, source and fate of dissolved organic matter (DOM) in a pilot-scale membrane bioreactor, Environ. Sci. Technol. 43 8821–8826.

Menniti, A., S. Kang, M. Elimelech, E. Morgenroth, 2009. Influence of shear on the production of extracellular polymeric substances in membrane bioreactors, Water Res. 43 4305–4315.

Metzger, U., P. Le-Clech, R.M. Stuetz, F.H. Frimmel, V. Chen, 2007. Characterisation of polymeric fouling in membrane bioreactors and the effect of different filtration modes, J. Membr. Sci. 301 180–189.

Min, K.-N., Ergas, S.J., Mermelstein, A., 2008. Impact of dissolved oxygen concentration on membrane filtering resistance and soluble organic matter characteristics in membrane bioreactors, Water Sci. Technol. 57 (2) 161–165.

Miyoshi, T., Tsuyuhara, T., Ogyu, R., Kimura, K., Watanabe, Y., 2009. Seasonal variation in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater, Water Res. 43 5109–5118.

Mohammadi, T., Kazemimoghadam, M., Saadabadi, M., 2003. Modelling of membrane fouling and flux decline in reverse osmosis during separation of oil in water emulsions, Desalination 157, 369–375.

Monclus, H., Ferrero, G., Buttiglieri, G., Comas, J., Rodriguez-Roda, I., 2011. Online monitoring of membrane fouling in submerged MBRs. Desalination 277 414-419.

Moreau, A., Ferreira, M.L., van Nieuwenhuijzen, A., van der Graaf, J., 2009. Overview of MBR activated sludge filterability at European scale, in: Presented at 5th IWA-MTC, Beijing, September 1–3, 2009.

Muller E.B., Stouthamer A.H., Vanverseveld H.W., Eikelboom D.H., 1995. Aerobic domestic wastewater treatment in a pilot-plant with complete sludge retention by cross-flow filtration. Water Res 29, 1179.

Nagaoka, H., Kono, S., Hamaya, S., 2001. Fouling mechanism considering production of utilization- and biomass-associated extracellular polymers in membrane bioreactor, in: Preprints IWA 2nd World Water Congress, Berlin, 2001, p. 1132.

Nagaoka, H., Ueda, S., Miya, A., 1996. Influence of bacterial extracellular polymers on the membrane separation activated sludge process, Water Sci. Technol. 34 (9) 165–172.

Nataraj, S., Schomäcker, R., Kraume, M., Mishra, I.M., Drews, A., 2008. Analyses of polysaccharide fouling mechanisms during crossflow membrane filtration, J. Membr. Sci. 308 152–161.

Ndinisa N.V., A.G. Fane, D.E. Wiley, D.F. Fletcher, 2006. Fouling control in a submerged flat sheet membrane system: Part II-Two-phase flow characterization and CFD simulations, Sep. Sci. Technol. 41 1411–1445.

Ng H.Y., Hermanowicz S.W., 2005. Membrane bioreactor operation at short solid retention times: performance and biomass characteristics, Water Res 39, 981-992.

Ng, A.N.L., Kim, A.S., 2008. A mini-review of modeling studies on membrane bioreactor (MBR) treatment for municipal wastewaters. Desalination 212, 261-281.

Ng, C.A., Sun, D., Fane, A.G., 2008. Operation of membrane bioreactor with powdered activated carbon addition. Separation Science and Technology 41 (7), 1447-1466.

Ng, K.K., Lin, C.F., Shaik, K.L., Panchangam, S.C., Hong, A.P. K., Yang, P.Y., 2010. The effect of soluble microbial products on membrane fouling in a fixed carrier biological system. Separation and Purification Technology 72 (1), 98-104.

Ngo, H.H., W. Guo, W. Xing, 2008. Evaluation of a novel sponge-submerged membrane bioreactor (SSMBR) for sustainable water reclamation, Bioresource Technol. 99 2429–2435.

Ni, B.-J., Fang, F., Xie, W.-M., Sun, M., Sheng, G.-P., Li, W.-H., Yu, H.-Q., 2009. Characterization of extracellular polymeric substances produced by mixed microorganisms in activated sludge with gel-permeating chromatography, excitation-emission matrix fluorescence spectroscopy measurement and kinetic modelling, Water Res. 43 1350–1358.

Ni, B.J., Zheng, R.J., Fang, F., Xie, W.M., Sheng, Q.P., Yu, H.Q., 2010. Fractionating soluble microbial products in the activated sludge process. Water Research 44 (7), 2292-2302.

Nywening, J.-P., Zhou, H., 2009. Influence of filtration conditions on membrane fouling and scouring aeration effectiveness in submerged membrane bioreactors to treat municipal wastewater, Water Res. 43 3548–3558.

Ognier, S., Wisniewski, C., Grasmick, A., 2004. Membrane bioreactor fouling in subcritical filtration conditions: a local critical flux concept, J. Membr. Sci. 229 171–177.

Okamura, D., Mori, Y., Hashimoto, T., Hori, K., 2009. Identification of biofoulant of membrane bioreactors in soluble microbial products. Water Research 43 (17), 4356-4362.

Ottoson, J., Hansen, A., Bjorlenius, B., Norder, H., Stenstrom, T.A., 2006. Removal of viruses, parasitic protozoa and microbial indicators in conventional and membrane processes in a wastewater pilot plant. Water Res. 40 1449-1457.

Pan, J.R., Su, Y., Chihpin, H., 2010. Characteristics of soluble microbial products in membrane bioreactor and its effect on membrane fouling. Desalination 250 (2), 778-780.

Pan, J.R., Sun, Y., Huang, C., 2009. Characteristics of soluble microbial products in membrane bioreactor and its effect on membrane fouling, Desalination 250 778–780.

Panglish, S., Gimbel, R., 2004. Formation of Layers of Non-Brownian Particles in Capillary Membranes Operated in Dead-End Mode, J. Chinese Inst. Chem.Eng. 35 (1), 77.

Passow, U., 2002. Transparent exopolymer particles (TEP) in aquatic environments. Progress in Oceanography 55, 287-333.

Passow, U., Alldredge, A.L., 1995. A dye-binding assay for the spectrophotometric measurement of transparent exopolymer particles (TEP), Limnol. Oceanogr. 40 (7) 1326–1335.

Pirbazari, M., Ravindran, V., Badriyha, B.N., Kim, S., 1996. Hybrid membrane filtration process for leachate treatment. Water Research 30 (11), 2691-2706.

Pollet, S., Guigui, C., Cabassud, C., 2009. Influence of intermittent aeration and relaxation on a side-stream membrane bioreactor for municipal wastewater treatment. Desalination 6, 108-118.

Pollice, A., Laera, G., 2005. Effects of complete sludge retention on biomass build-up in a membrane bioreactor, Water Sci Technol 52, 369-375.

Pollice, A., Laera, G., Blonda, M., 2004. Biomass growth and activity in a membrane bioreactor with complete sludge retention, Water Res. 38, 1799-1808.

Pollice, A., Brookes, A., Jefferson, B., Judd, S., 2005. Sub-critical flux fouling in membrane bioreactors—a review of recent literature, Desalination 174 221–239.

Prieske H., L. Böhm, A. Drews, M. Kraume, 2010. Optimised hydrodynamics for membrane bioreactors with immersed flat sheet membrane modules, Desalination Water Treatm. 18 270–276.

Radjenovic, J., Petrovic, M., Barcelo, D., 2009. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Res., 43, 831-841.

Ramesh, A., Lee, D.J., Wang, M.L., Hsu, J.P., Juang, R.S., Hwang, K.J., Liu, J.C., Tseng, S.J., 2006. Biofouling in membrane bioreactor. Separation and Science Technology 41 (7), 1345-1370.

Reif, R., Suárez, S., Omil, F., Lema, J. M., 2008. Fate of pharmaceuticals and cosmetic ingredients during the operation of a MBR treating sewage. Desalination, 221(1–3), 511-517.

Reinthaler, F.F., Posch, J., Feierl, G., Wüst, G., Haas, D., Ruckenbauer, G., Mascher, F., Marth, E., 2003. Antibiotic resistance of E. coli in sewage and sludge, Water Res. 37(8), 1685-1690.

Remy, M., van der Marel, P., Zwijnenburg, A., Rulkens, W., Temmink, H., 2009. Low dose powdered activated carbon addition at high sludge retention times to reduce fouling in membrane bioreactors. Water Research 43 (2), 345-350.

Rochex A., J.J. Godon, N. Bernet, R. Escudié, 2008. Role of shear stress on composition, diversity and dynamics of biofilm bacterial communities, Water Res. 42 4915–4922.

Rosal, R., Rodríguez, A., Perdigón-Melón, J. A., Petre, A., García-Calvo, E., Gómez, M. J., Fernández-Alba, A. R., 2010. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. Water Research, 44(2), 578-588.

Rosenberger S., Kraume M., 2002. Filterability of activated sludge in membrane bioreactors, Desalination 146, 373-379.

Rosenberger S., Kruger U., Witzig R., Manz W., Szewzyk U., Kraume M., 2002. Performance of a bioreactor with submerged membranes for aerobic treatment of municipal waste water, Water Res 36, 413.

Rosenberger S., Witzig R., Manz W., Szewzyk U., Kraume M., 2000. Operation of different membrane bioreactors: experimental results and physiological state of the microorganisms, Water Sci Technol 41, 269–77.

Rosenberger, S., Evenblij, H., te Poele, S., Wintgens, T., Laabs, C., 2005. The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes—six case studies of different European research groups, J. Membr. Sci. 296 113–126.

Rosenberger, S., Kraume, M., 2002. Filterability of activated sludge in membrane bioreactors, Desalination 146 373–379.

Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, G., Jekel, M., Schrotter, J.-C., 2006. Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment, Water Res. 40 710–720.

Ross W.R., Barnard J.P., Strohwald N.K.H., Grobler C.J., Sanetra J., 1992. Practical application of the ADUF process to the full-scale treatment of a maize-processing effluent, Water Sci. Technol. 25(10), 27-39.

Sagbo O., Y. Sun, A. Hao, P. Gu, 2008. Effect of PAC addition on MBR process for drinking water treatment, Sep. Purif. Technol. 58 320–327.

Sakai Y., Fukase T., Yasui H., Shibata M., 1997. An activated sludge process without excess sludge production, Wat. Sci. Technol. 36, 163-170.

Santos, A., Ma, W., Judd, S., 2011. Membrane bioreactors: Two decades of research and implementation. Desalination 273 148-154.

Saroj, D.P., Guglielmi, G., Chiarani, D., Andreottola, G., 2008. Modeling and simulation of membrane bioreactors by incorporating simultaneous storage and growth concept: an especial attention to fouling while modeling the biological process, Desalination 221 475–482.

Scannapieco, D., Naddeo, V., Belgiorno, V., 2012. MBR technology: its main characteristics and market over the world. SIDISA – International Symposium of Sanitary and Environmental Engineering, 26-29 June 2012, Milan, Italy.

Scannapieco, D., Naddeo, V., Belgiorno, V., 2013. Control of fouling in MBRs through nanospheres addition. CEST2013, Athens, Greece.

Schaller J., A. Drews, M. Kraume, 2006. Analyses and modelling of filtration processes in MBR and test cells, Desalination 199 507–508.

Sethi, S., Wiesner Mark, R., Dennis, E., 2001. Optimization of hollow-fiber design and low-pressure membrane system operation, J. Environ. Eng. 127 (6), 485.

She, Q., Tang, C.Y., Wang, Y.-N., Zhang, Z., 2009. The role of hydrodynamic conditions and solution chemistry on protein fouling during ultrafiltration, Desalination 249 1079–1087.

Simmons, F.J., Kuo, D.H.W., Xagoraraki, I., 2011. Removal of human enteric viruses by a full-scale membrane bioreactor during municipal wastewater processing. Water Res. 45 (2011) 2739-2750.

Smith C.V., Gregorio D., Talcott R.M. (1969). The use of ultrafiltration membranes for activated sludge separation. Proceedings of the 24th Annual Purdue Industrial Waste Conference. Purdue University, Lafayette, Indiana, USA.

Smith, P.J., S. Vigneswaran, H.H. Ngo, H. Nguyen, R. Ben-Aim, 2006. Application of an automation system and a supervisory control and data acquisition (SCADA) system for the optimal operation of a membrane adsorption hybrid system, Water Sci. Technol. 53 179–184.

Smith P.J., S. Vigneswaran, H.H. Ngo, R. Ben-Aim, H. Nguyen, Design of a generic control system for optimising back flush durations in a submerged membrane hybrid reactor, J. Membr. Sci. 255 (2005) 99–106.

Snyder, S. A., Adham, S., Redding, A. M., Cannon, F. S., DeCarolis, J., Oppenheimer, J., Yoon, Y., 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination, 202(1–3), 156-181.

Sofia A., W.J. Ng, S.L. Ong, 2004. Engineering design approaches for minimum fouling in submerged MBR, Desalination 160 2004 67–74.

Sombatsompop, K., Visvanathan, C., Ben Aim, R., 2006. Evaluation of biofouling phenomenon in suspended and attached growth membrane bioreactor systems, Desalination 201 138–149.

Song K.G., Y. Kim, K.-H. Ahn, 2008. Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor, Desalination 221 467–474.

Song, K.G., Choung, Y.K., Ahn, K.H., Cho, J., Yun, H., 2003. Performance of membrane bioreactor system with sludge ozonation process for minimization of excess sludge production, Desalination 157, 353–359 .

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

Suárez, S., Ramil, M., Lema, J. M., 2005. Removal of pharmaceutically active compounds in nitrifying-denitrifying plants. Water Science and Technology, 52, 9.

Sun D.D., Hay C.T., Khor S.L., 2006. Effects of hydraulic retention time on behavior of start-up submerged membrane bioreactor with prolonged sludge retention time, Desalination 195, 209–225.

Sun, F.-Y., Wang, X.-M., Li, X.-Y., 2008. Visualisation and characterisation of biopolymer clusters in a submerged membrane bioreactor, J. Membr. Sci. 325 691–697.

Szewzyk, U., Szewzyk, R., Manz, W., Schleifer, K.H., 2000. Microbiological safety of drinking water. Annual Review of Microbiology 54, 81-127.

Tadkaew, N., Sivakumar, M., Khan, S. J., McDonald, J. A., Nghiem, L. D., 2011. Effect of mixed liquor pH on the removal of trace organic contaminants in a membrane bioreactor. Bioresource Technology, 101(5), 1494-1500.

Tay J.H., P. Yang, W.Q. Zhuang, S.T.L. Tay, Z.H. Pan, 2007. Reactor performance and membrane filtration in aerobic granular sludge membrane bioreactor, J. Membr. Sci. 304 24–32.

Tchobanoglous G., Burton F. L., Stensel H. D. (2003). Wastewater engineering: treatment and reuse, 3rd ed., Metcalf & Eddy, McGraw-Hill, New York.

Teychene, B., Guigui, C., Cabassud, C., 2011. Engineering of an MBR supernatant fouling layer by fine particles addition: a possible way to control cake compressibility. Water Research 45, 2060-2072.

Thanh, B.X., Spérandio, M., Guigui, C., Ben Aim, R., Wan, J., Visvanathan, C., 2010. Coupling sequencing batch airlift reactor (SBAR) and membrane filtration: influence of nitrate removal on sludge characteristics, effluent quality and filterability, Desalination 250 850–854.

Thiemig C., T. Murakami, T. Itokawa, Influence of polymer addition on flux and biological performance of a municipal membrane bioreactor, in: IWA Regional Conference for Membrane Technologies in Water and Waste Water Treatment, Moscow, June 3–6, 2008.

Trussell, R.S., Jang, N., Merlo, R.P., Kim, I.S., Hermanowicz, S.W., Jenkins, D., 2009. Changes in mixed liquor and organic foulant properties affect membrane fouling for non-nitrifying and nitrifying conditions, Water Environ. Res. 81 255–264.

Trussell, R.S., Merlo, R.P., Hermanowicz, S.W., Jenkins, D., 2006. The effect of organic loading on process performance and membrane fouling in a submerged membrane bioreactor treating municipal wastewater, Water Res. 40 2675–2683.

Ueda, T., Hata, K., Kikuoka, Y., 1997. Treatment of domestic sewage from rural settlements by a membrane bioreactor, Water Sci. Technol. 34 (9), 189-196.

Van de Ven W.J.C. van't Sant K., Punt I.G.M., Zwijnenburg A., Kemperman A.J.B., van der Meer W.G.J., Wessling M., 2008. Hollow fiber dead-end ultrafiltration: Influence of ionic environment on filtration of alginates, J. Membr. Sci. 308, 218-229.

Van den Brink, P., Zwijnenburg, A., Smith, G., Temmink, H., van Loosdrecht, M., 2009. Effect of free calcium concentration and ionic strength on alginate fouling in cross-flow membrane filtration, J. Membr. Sci. 345 207–216.

Van den Broeck, R., Van Dierdonck, J., Caerts, B., Bisson, I., Kregersman, B., Nijskens, P., Dotremont, C., Van Impe, J.F., Smets, I.Y., 2010. The impact of deflocculation–reflocculation on fouling in membrane bioreactors, Sep. Purif. Technol. 71 279–284.

Van der Gast, C.J., Jefferson, B., Reid, E., Robinson, T., Bailey, M.J., Judd, S.J., Thompson, I.P., 2006. Bacterial diversity is determined by volume in membrane bioreactors, Environ. Microbiol. 8 (6) 1048–1055.

Van der Marel, P., Zwijnenburg, A., Kemperman, A., Wessling, M., Temmink, H., van der Meer, W., 2009. An improved flux-step method to determine the critical flux and the critical flux for irreversibility in amembrane bioreactor, J. Membr. Sci. 332 24–29.

Van Loosdrecht, M.C.M., Henze, M., 1999. Maintenance, endogenous respiration, lysis, decay and predation, Water Sci Technol 39, 107-117.

Van Nevel, S., Hennebel, T., De Beuf, K., Du Laing, G., Verstraete, W., Boon, N., 2012. Transparent exopolymer particle removal in different drinking water production centers. Water Research 46, 3603-3611.

Vela, M.C.V., Alvarez Blanco, S., Lora Garcıa, J., Rodrıguez, E.B., 2008. Analysis of membrane pore blocking models applied to the ultrafiltration of PEG, Separation and Purification Technology 62, 489–498.

Verrecht, B., Judd, S., Guglielmi, G., Brepols, C., Mulder, J.W., 2008. An aeration energy model for an immersed membrane bioreactor, Water Res. 42 4761–4770.

Villacorte, L.O., Kennedy, M.D., Amy, G.L., Schippers, J.C., 2009. Measuring transparent exopolymer particles (TEP) as indicator of the (bio)fouling potential of RO feed water. Desalination and Water Treatment 5, 207-212.

Villacorte, L.O., Schurer, R., Kennedy, M.D., Amy, G.L., Schippers, J.C., 2010. The fate of transparent exopolymer particles (TEP) in seawater UF-RO system: a pilot plant study in Zeeland, The Netherlands. Desalination and Water Treatment 13, 109-119.

Wang, J.C., Park, J.K., Whang, L.M. 2001. Comparison of fatty acid composition and kinetics of phosphorus-accumulating organisms and glycogen-accumulating organisms. Water Environ. Res. 73, 704-710.

Wang X.M., T.D. Waite, 2008. Impact of gel layer formation on colloid retention in membrane filtration processes, J. Membr. Sci. 325 486–494.

Wang, Z.W., Y. Liu, J.-H. Tay, 2005. Distribution of EPS and cell surface hydrophobicity in aerobic granules, Appl. Microbiol. Biotechnol. 69 469–473.

Wang, X.M., Li, X.-Y., 2008. Accumulation of biopolymer clusters in a submerged membrane bioreactor and its effect on membrane fouling, Water Res. 42 855–862.

Wang, Z., Wu, Z., Tang, S., 2009. Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor, Water Res. 43 2504–2512.

Wang, Z., Wu, Z., Yin, X., Tian, L., 2008. Membrane fouling in a submerged membrane bioreactor (MBR) under sub-critical flux operation: membrane foulant and gel layer characterization, J. Membr. Sci. 325 238–244.

Wedi, D., 2003. Design and operating results of full scale MBR in Germany, in: Proceedings of the IWA-LET Noordwijk, May 2003.

Wei Y., Van Houten R.T., Borger A.R., Eikelboom D.H., Fan Y. (2003). Minimization of excess sludge production for biological wastewater treatment, Water Res 37, 4453-4467.

Wicaksana F., A.G. Fane, A.W.K. Law, 2009. The use of constant temperature anemometry for permeate flow distribution measurement in a submerged hollow fiber system, J. Membr. Sci. 339 195–203.

Williams, M.D., Pirbazari, M., 2007. Membrane bioreactor process for removing biodegradable organic matter from water. Water Res. 41 3880-3893.

Williams, M.M., Braun-Howland, E.B., 2003. Growth of Escherichia coli in model distribution system biofilms exposed to hypochlorous acid or monochloramine. Applied and Environmental Microbiology 69, 5463-5471.

Wisniewski, C., Grasmick, A., 1998. Floc size distribution in a Membrane Bioreactor and consequences for membrane fouling, Colloids Surf. A 138, 403.

Wozniak, T., 2009. MBR design and operation using MPE-technology (membrane performance enhancer), Desalination 250 723–728.

Wu, Z., Wang, Z., Huang, S., Mai, S., Yang, C., Wang, X., Zhou, Z., 2008. Effects of various factors on critical flux in submerged membrane bioreactors for municipal wastewater treatment, Sep. Purif. Technol. 62 56–63.

Xing C.H., Tardieu E., Qian Y., Wen W.H., 2000. Ultrafiltration membrane bioreactor for urban wastewater reclamation, J. Membr. Sci. 177, 73–82.

Yang, P.Y., Cao, K., Kim, S.J., 2002. Entrapped Mixed Microbial Cell Process for combined secondary and tertiary wastewater treatment. Water Environment Research. 74, 226.

Yang, S.-F., Li, X.-Y., 2009. Influences of extracellular polymeric substances (EPS) on the characteristics of activated sludge under non-steady-state conditions, Process. Biochem. 44 91–96.

Yang, W., Cicek, N., Ilg, J., 2006. State-of-the-art of membrane bioreactors: worldwide research and commercial applications in North America, J. Membr. Sci. 270 (1–2) 201–211.

Ye, Y., Le-Clech, P., Chen, V., Fane, A.G., Jefferson, B., 2005. Fouling mechanisms of alginate solutions as model extracellular polymeric substances, Desalination 175 7–20.

Yeo A.P.S., A.W.K. Law, A.G. Fane, 2007. The relationship between performance of submerged hollow fibers and bubble-induced phenomena examined by particle image velocimetry, J. Membr. Sci. 304 125–137.

Yeom I. T., Lee K. R., Choi Y. G., Kim H. S., Kwon J. H., Lee U. J., Lee Y. H., 2005. A pilot study on accelerated sludge degradation by a high-concentration membrane bioreactor coupled with sludge pretreatment, Water Sci. Tech. 52, 201-210.

Yeon K.M., C.H. Lee, J. Kim, 2009. Magnetic enzyme carrier for effective biofouling control in the membrane bioreactor based on enzymatic quorum quenching, Environ. Sci. Technol. 7403-7409.

Yoon, K.H., Yeon, K.M., Lee, C.H., Lee, S.H., Swaminathan, T., 2006. Biofilm structure and extracellular polymeric substances in low and high dissolved oxygen membrane bioreactors, Sep. Sci. Technol. 41 (7) 1213–1230.

Yu H.Y., L.-Q. Liu, Z.-Q. Tang, M.-G. Yan, J.-S. Gu, X.-W.Wei, 2009. Mitigated membrane fouling in an SMBR by surface modification, J. Membr. Sci. 310 409–417.

Yun, M.A., Yeon, K.M., Park, J.S., Lee, C.H., Chun, J.S., Lim, D.J., 2006. Characterization of biofilm structure and its effect on membrane permeability in MBR for dye wastewater treatment, Water Res. 40 (1) 45–52.

Zanetti, F., de Luca, G., Sacchetti, R., 2010. Performance of a full-scale membrane bioreactor system in treating municipal wastewater for reuse purposes. Bioresource Technol. 101 3768-3771.

Zator, M., Ferrando, M., Lopez, F., Güell, C., 2006. Characterization of foulant removal by confocal scanning laser microscopy, Desalination 200 203–204.

Zator, M., Ferrando, M., López, F., Güell, C., 2007. Membrane fouling characterization by confocal microscopy during filtration of BSA/dextran mixtures, J. Membr. Sci. 301 57–66.

Zhang, J., Chua, H.C., Zhou, J., Fane, A.G., 2006. Factors affecting the membrane performance in submerged membrane bioreactors, J. Membr. Sci. 284 54–66.

Zhang, Y., Geißen, S., Gal, C., 2008. Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies. Chemosphere, 73(8), 1151-1161.

Zhou, W., Wu, B., She, Q., Chi, L., Zhang, Z., 2009. Investigation of soluble microbial products in a full-scale UASB reactor running at low organic loading rate. Bioresource Technology 100 (14), 3471-3476.