Dipl.-Ing. Vera Iversen

Comprehensive assessment of flux enhancers in membrane bioreactors for wastewater treatment
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Acknowledgement

This work was carried out at the Chair of Chemical and Process Engineering at the Technische Universität Berlin as part of the EU FP 6 project “AMEDEUS” (contract number: 018328). I would like to acknowledge the European Commission for the financial support. I would also like to thank all the project partners for the interesting discussions, valuable input, and support for my work. Especially our project coordinator Boris Lesjean with his strong personal commitment to this project and the KompetenzZentrum Wasser Berlin for doing a great job in organising, coordinating and communicating are thanked. The University of New South Wales is gratefully acknowledged for their financial support and the opportunity to present my work at the IMSTEC in Sydney. Also the producers of the various tested additives are thanked, for their help in choosing promising substances and granting me free samples of the chemicals.

I am very grateful to my supervising Professor Mr. Kraume. Without the regular rapports, the critical discussions and his confidence in my research this work would not have been the same. Not to forget the work of my assessors Professor Melin and especially Professor Drews, for her untiringly support of my academic research.

For the great (working) atmosphere, their always helpful advice and feed-back on my work I would like to thank all my colleagues, especially Ute Bracklow, Jochen Grünig, Helmut Prieske, Jana Schaller, Daniel Stumpf, Teresa de la Torre Garcia and Martin Vocks. Also the work of my students Djihan Beuter, Loïc Bonnet, Nils Goldammer, Gesine Götz, Samuel Groß, Verena Lößfler, Juliane Mohaupt, Johannes Münz, Youssef Rannane, Tino Schmidt and Stefanie Wieden is acknowledged. I really enjoyed working with you! I am very happy I could spend some month with our guest PhD students and post-docs Christian Antileo, Fangang Meng, Hasan Koseoglu and Nevzat Ö. Yigit who contributed to a large extent to my MBR knowledge and research but also to my cultural understanding.

The construction and maintenance of the pilot system in such a short time would not have been possible without the help of Werner Alborn, Rainer Schwarz and their team. While working with a 3 m³ pilot system was not always easy, the presence and great help of Andrea Hasselmann, Stephanie Herrmann and Jörn Villwock delightfully lightened my sludgy days. Thank you all very much for your crucial labour and assistance with “Wolferl” and “Nannerl”.

I am exceptionally grateful for the support of my parents Renate and Hans-Christian, my brother Thomas (who patently answered all my IT questions) and my in-laws. Thank you for taking Paula every now and then!

The love and unconditional support of my husband Patrick, his patience and understanding strongly encouraged me and helped me during difficult moments. I did not take it for granted that you joined my frequent weekend and holiday checks on my pilots! Last but not least I want to thank my daughter Paula. Though work disturbances do not seem to be the most common way of support, she greatly focused me and motivated me to do night shifts. I am so happy you joined our lives!
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## Nomenclature

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<th>Meaning</th>
<th>Dimension</th>
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<tbody>
<tr>
<td>AOX</td>
<td>adsorbable organohalogens</td>
<td></td>
</tr>
<tr>
<td>CAS</td>
<td>conventional activated sludge</td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>cross flow</td>
<td></td>
</tr>
<tr>
<td>CIP</td>
<td>cleaning in place</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>chemical oxygen demand</td>
<td>mgL⁻¹</td>
</tr>
<tr>
<td>COP</td>
<td>cleaning out of place</td>
<td></td>
</tr>
<tr>
<td>CST</td>
<td>capillary suction time</td>
<td>s</td>
</tr>
<tr>
<td>DNR</td>
<td>denitrification rate</td>
<td>mgNh⁻¹gvSS⁻¹</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
<td>mgL⁻¹</td>
</tr>
<tr>
<td>EEM</td>
<td>excitation-emission matrix</td>
<td></td>
</tr>
<tr>
<td>EPS</td>
<td>extracellular polymeric substances</td>
<td></td>
</tr>
<tr>
<td>FE</td>
<td>Flux enhancer</td>
<td></td>
</tr>
<tr>
<td>FS</td>
<td>flat sheet</td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td>granular activated carbon</td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>hollow fibre</td>
<td></td>
</tr>
<tr>
<td>HFO</td>
<td>heated ferric oxide</td>
<td></td>
</tr>
<tr>
<td>HRT</td>
<td>hydraulic retention time</td>
<td>h</td>
</tr>
<tr>
<td>LC-OCD</td>
<td>liquid chromatography with organic carbon detection</td>
<td></td>
</tr>
<tr>
<td>NOM</td>
<td>natural organic matter</td>
<td>mgL⁻¹</td>
</tr>
<tr>
<td>NR</td>
<td>nitrification rate</td>
<td>mgNh⁻¹gvSS⁻¹</td>
</tr>
<tr>
<td>MBR</td>
<td>membrane bioreactor</td>
<td></td>
</tr>
<tr>
<td>MLSS</td>
<td>mixed liquor suspended solids</td>
<td>gL⁻¹</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
<td>Da</td>
</tr>
<tr>
<td>OUR</td>
<td>oxygen uptake rate</td>
<td>mgL⁻¹s⁻¹</td>
</tr>
<tr>
<td>PAC</td>
<td>powdered activated carbon</td>
<td></td>
</tr>
<tr>
<td>PACl</td>
<td>polyaluminium chloride</td>
<td></td>
</tr>
<tr>
<td>PAN</td>
<td>polyacrylonitrite</td>
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<tr>
<td>PE</td>
<td>polyethylene</td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>polysulfone</td>
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</tr>
</tbody>
</table>
PFS  | polymeric ferric sulphate
PR  | protein
PS  | polysaccharide
PSD | particle size distribution
PVDF | polyvinylidene fluoride
SEC | size exclusion chromatography
SMP | soluble microbial products
SRT | sludge retention time  \( \text{d} \)
SVI | sludge volume index  \( \text{mLmg}^{-1} \)
TEP | transparent exopolymer particles
TMP | transmembrane pressure  \( \text{bar} \)
TOC | total organic carbon
ww | wastewater

**Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Dimension</th>
</tr>
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<tr>
<td>A</td>
<td>area</td>
<td>( \text{m}^2 )</td>
</tr>
<tr>
<td>c</td>
<td>concentration</td>
<td>( \text{mgL}^{-1} )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>difference</td>
<td>-</td>
</tr>
<tr>
<td>d</td>
<td>diameter</td>
<td>( \text{m} )</td>
</tr>
<tr>
<td>df</td>
<td>fractal dimension</td>
<td>-</td>
</tr>
<tr>
<td>DO</td>
<td>dissolved oxygen concentration</td>
<td>( \text{mgL}^{-1} )</td>
</tr>
<tr>
<td>J</td>
<td>flux</td>
<td>( \text{Lm}^{-1}\text{h}^{-1} )</td>
</tr>
<tr>
<td>( k_{La} )</td>
<td>oxygen transfer coefficient</td>
<td>( \text{s}^{-1} )</td>
</tr>
<tr>
<td>( \mu )</td>
<td>dynamic viscosity</td>
<td>( \text{mPa s} )</td>
</tr>
<tr>
<td>MLSS</td>
<td>concentration of mixed liquor suspended solids</td>
<td>( \text{gL}^{-1} )</td>
</tr>
<tr>
<td>n</td>
<td>number</td>
<td>-</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>nitrate concentration</td>
<td>( \text{mgNO}_3\text{-N L}^{-1} )</td>
</tr>
<tr>
<td>v</td>
<td>velocity</td>
<td>( \text{ms}^{-1} )</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>( \text{m}^3 )</td>
</tr>
<tr>
<td>R</td>
<td>filtration resistance</td>
<td>( \text{m}^{-1} )</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>( \text{s} )</td>
</tr>
<tr>
<td>TMP</td>
<td>transmembrane pressure</td>
<td>( \text{bar} )</td>
</tr>
<tr>
<td>( \dot{V} )</td>
<td>flow rate</td>
<td>( \text{Lh}^{-1} )</td>
</tr>
<tr>
<td>Subscript</td>
<td>Meaning</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------------</td>
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</tr>
<tr>
<td>A</td>
<td>adsorption</td>
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</tr>
<tr>
<td>blank</td>
<td>reference</td>
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<tr>
<td>CF</td>
<td>cross flow</td>
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<tr>
<td>crit</td>
<td>critical</td>
<td></td>
</tr>
<tr>
<td>exo</td>
<td>exogenous</td>
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<tr>
<td>endo</td>
<td>endogenous</td>
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</tr>
<tr>
<td>FC</td>
<td>filter cake</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>membrane</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>particle</td>
<td></td>
</tr>
<tr>
<td>PB</td>
<td>pore blocking</td>
<td></td>
</tr>
<tr>
<td>tot</td>
<td>total</td>
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</tr>
<tr>
<td>treat</td>
<td>treated</td>
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</table>
1 Introduction

Due to increasingly stringent legislative demands on water quality, membrane bioreactors (MBR) are considered as one of the most promising techniques for wastewater treatment. The number of installations – for industrial as well as municipal application – has increased dramatically over the last ten years (Lesjean and Huisjes, 2008).

Fouling, however, still is a non-resolved problem. Although a large number of all MBR publications deal with fouling (Kraume and Drews, 2009; Meng et al., 2009), the complex interactions of membrane material, sludge properties and operational conditions are not fully understood (Drews et al., 2006; 2007; Meng et al., 2009), especially since the filtration systems, applications and analytical methods vary widely (Rosenberger et al., 2005).

Traditional strategies for fouling prevention include the improvement of hydrodynamic conditions, air scour and backwash or filtration break. Innovative methods include the modification of the membrane by plasma treatment (Yu et al., 2007) or nanocoating (Bae et al., 2006), the electromagnetic deflection of charged coarse particles (Chen et al., 2007), the modification of the suspension by the use of granulated sludge for seeding (Li et al., 2007) and the addition of sponge-like carrier particles (Yang et al., 2006a). Also the addition of certain chemicals for coagulation, flocculation and/or adsorption has recently been reported to modify the sludge towards a better filterability. This approach offers a variety of possibilities and advantages but systematic studies are still necessary. Especially the use of metal coagulants, cationic polymers and powdered activated carbon (PAC) is often recommended for flux enhancement in MBR.

While metal coagulants offer additional advantages such as an improved phosphorous removal, they might also impact the pH and thus the microbial activity (Song et al., 2008). The effect of synthetic polymers on sludge filterability has been closely examined and positive effects were found (Qiu, 2005; Yoon and Collins, 2006; Hwang et al., 2007; Koseoglu et al., 2008). Also natural polymers such as chitosan can improve the sludge filterability (Ji et al., 2008).

Adsorption on activated carbon shows significant improvements for the MBR operation, while a reduction of fouling is reported in several studies (Li et al., 2005; Fang et al., 2006). These systems also exhibit a better or more stable carbon removal (Guo et al., 2006; Munz et al., 2007) and are able – under certain circumstances – to buffer the effects of toxic compounds (Lesage et al., 2008).

This thesis summarizes the state-of-the-art of flux enhancement in MBR and presents the outcomes of several own studies that were conducted with different chemicals. Their impact on filterability, supernatant compounds, mixed liquor properties such as apparent viscosity and particle size and possible side effects on the microorganisms, nutrient removal and the membrane itself was evaluated in pre-studies and pilot plant trials as shown in Figure 1.
Pre-studies:


Pilot plant operation:

2 State-of-the-art: Fouling in MBR

2.1 Membrane bioreactors (MBR)

A membrane bioreactor or membrane assisted activated sludge process for wastewater treatment combines an activated sludge treatment with a membrane for the separation of the biological suspension. These membranes are usually in the micro- (MF) or ultra-filtration (UF) range and ensure a particle free effluent. In terms of effluent quality, an MBR thus exceeds the conventional activated sludge system with a gravity-driven clarifier for solid separation. According to, e.g., Drews and Kraume (2005), further advantages are:

- MBRs allow higher biomass concentrations and thus higher metabolic rates. The same inflow can be treated in a smaller reactor with smaller footprint than a conventional system.
- An additional variable for process control is available as hydraulic and solid retention times are independent of each other.
- The system is almost independent of sludge settling properties (filamentous bacteria, foam to some extent).
- High sludge ages are possible and thus less excess sludge is produced.

When the MBR technology first emerged in the late 1960s, its high maintenance and operation costs (especially for the membranes and the circulation pumps) made it only attractive for specialised applications, e.g. the treatment of ship-board sewage or high strength industrial wastewaters. With improvements in membrane material and production, research in the field of fouling and its mitigation, as well as the shift from external to submerged membranes, the technology has become competitive over the last decades (Judd, 2006; Lesjean and Huisjes, 2008).

On the other hand, increasing legislative demands as well as water stress put further pressure on the development of high quality effluent processes. For the European market, the 1976 European bathing water directive shall be mentioned here which was replaced by a new and more demanding directive in 2006. Also the Urban Waste Water Treatment Directive, defining nutrient discharge limits and even lower limits for so called ‘Sensitive Areas’, further boosted the MBR technology. While legislation has long been the driving force for the development of advanced water treatment technologies in Europe and North America, it now becomes increasingly influential in emerging markets as India and China (MembraneTechnology, 2008).

With increasing water stress in the arid regions of Asia Pacific, the Middle East, parts of South Africa, North America and Southern Europe the need for water reclamation and reuse increases. An overview of the actual and potential role of water reuse in Europe is given by Hochstrat et al. (2008a; 2008b). Furthermore, the government of Singapore has decided to allow the direct re-use of treated wastewater as potable water. 3.5 % of Singapore’s daily drinking water consumption shall thus be provided by 2011 (Lee, 2005). A similar approach is already taken in Windhoek in Namibia where even 30-50 % of the daily potable water requirements are thus met (Asano et al., 2007).

Due to the thus increasing demands on sophisticated wastewater treatment technologies it is not astonishing that the global market for MBR is expected to grow with an annual rate of 10.5 % increasing in value from US$ 296 million in 2008 to US$ 488 million by 2013. The sales of MBR systems is expected to grow faster than the gross domestic products of the countries...
installing them and more rapidly than the industries that use them (Hanft, 2008). A conclusive overview of the European MBR market, its trends and perspectives is given by Lesjean and Huisjes (2008).

Notwithstanding these advantages and the need for high quality effluent techniques, the energy costs of the MBR technology are still relatively high. According to Krause and Cornel (2007), approx. 50% of the energy is required for fouling control on the membrane surface (in terms of cross flow aeration). Fouling control in terms of hydrodynamic optimisation or minimisation of the fouling propensity of the sludge thus directly cuts down the operation costs. This fact is also reflected in literature where approximately 30% of all MBR publications deal with fouling (Yang et al., 2006b).

2.2 Fouling in MBR

By the term fouling, all physical phenomena are summarised that lead to a decrease in membrane permeability. According to Darcy’s Law the filtration can be described as:

\[ \text{TMP} = \frac{\mu_{\text{perm}}}{A} R_{\text{tot}} \frac{dV}{dt} \]  

(2.2.1)

In theory the total resistance \( R_{\text{tot}} \) can be split into several different resistances due to the formation of filter cake, pore blocking, adsorption within the membrane pores and the resistance of the membrane itself (as shown in Figure 2). Practically all except the last are summarised as fouling. As stated by Chang et al. (2002) fouling is mostly classified in categories of reversible (removable by physical action) and irreversible (only removable by chemical cleanings) fouling. However, this categorization is somewhat simplistic. Kraume et al. (2009) distinguish between cake fouling (removable by backflush or relaxation), residual fouling (removed by a maintenance cleaning), irreversible fouling (only removed by a main cleaning) and the long-term irreversible fouling of the membrane. This long-term irreversible fouling cannot be removed even by intensive chemical cleanings and leads to membrane aging finally necessitating module replacement. The clogging of the membrane module is generally not included in the definition of fouling as also shown in Figure 3. It is caused by larger suspended solids, especially hair and other debris that accumulate within the membrane module. Naturally, clogging affects especially hollow fibre (HF) modules that are potted at both ends while flat sheet (FS) systems are less prone to clogging. A careful pre-treatment of the influent can mostly beware the system of clogging.

![Figure 2: The different filtration resistances](Image)

Figure 2: The different filtration resistances
Despite the large number of publications dealing with this topic the mystery of fouling has still not been solved. This is due to the complexity of the system and interactions (depicted in Figure 3) including the unpredictable behaviour of the biomass.

As shown in Figure 3 there are certain engineering variables (INPUT parameters) such as membrane material and operation, hydraulic and sludge residence times (HRT and SRT), geometry and the feed that indirectly influence the OUTPUT variable permeability loss. At the same time, the INTERMEDIATE variables that characterise biomass and hydrodynamics and interact strongly with each other directly impact fouling and clogging behaviour of the system. These can hardly be directly influenced.

**INPUT:**
MBR Design and Operation

**Operation**
- Biological
  - SRT
  - HRT/loading rate/feed type temperature
  - DO/N; conc.
- Membrane
  - Dead end/crossflow (vel.)
  - Constant TMP/flux
  - Backpulsing/relaxation
  - Cleaning intervals/chemicals
- Reactor
  - Tank height
  - Cross section ratio
  - riser/downcomer
  - Module spacing
  - Module height
  - Bubble size/aeration ports
- Membrane
  - Pore size
  - Material
  - Hydrophilicity/charge
  - Surface roughness

**INTERMEDIATE:**
Biomass properties and hydrodynamics

**OUTPUT:**
Permeability Loss

According to Chang et al. (2002), the “nature and extent of fouling in MBRs is strongly influenced by three factors: biomass characteristics, operating conditions, and membrane characteristics”. The last two will only shortly be discussed within the next paragraphs, while the discussion of the biomass characteristics will be more detailed as these are influenced by the addition of flux enhancers.

### 2.2.1 Membrane characteristics

Several characteristics of the membrane material “such as pore size, porosity, surface energy, charge, roughness, and hydrophilicity/hydrophobicity, etc.” directly have an impact on the membrane fouling (Chang et al., 2002).

Generally there are two types of membrane materials: ceramic and polymeric materials. Ceramic membranes have several advantages like higher resistance concerning chemicals and temperature resulting in longer lifetime and better mechanical stability (backpulse at high TMP).
Nevertheless their application is usually restricted to specialised applications (e.g. treatment of industrial wastewater) as the material is difficult to produce and in the post-processing so that the investments costs are higher than for polymeric membranes (Melin and Rautenbach, 2004).

Most applications use synthetic polymeric membranes which can be customised by the usage of a broad range of different polymers or polymer blends. The structural characteristics are influenced by the molecular weight, the chemical structure and interactions between the macromolecules (Melin and Rautenbach, 2004).

Due to the hydrophobic interactions between the membrane and the biomass, hydrophilic membranes yield higher fluxes and are therefore favoured in the field of wastewater treatment (Chang et al., 2002; Kim et al., 2006). In order to hydrophilise naturally hydrophobic polymers such as PP, PE or PVDF the surface modification by plasma treatment has recently emerged (Batsch et al., 2005). Good results in the prevention of irreversible fouling were found for these membranes (Yu et al., 2005; Yu et al., 2007).

2.2.2 Operating conditions

The operating conditions include factors like the configuration (submerged or external), aeration, filtration mode (pulse/pause/back pulse and duration of each period), retention times and values for the constant flux or TMP operation. These factors will not all be discussed within the next pages but the most important factors will be targeted.

De Wever et al. (2009) developed a decision tree supporting the choice for a submerged or an external (where the module is submerged within an extra tank, also called side-stream) configuration.

According to their literature study the fouling in an external configuration is said to be lower as “hydraulics and fluid dynamics can be independently optimized in the separate filtration tank”. According to Gander et al. (2000) “the energy consumption of side-stream systems is usually two orders of magnitude higher than that of submerged systems”. Also the distribution of the costs strongly differs. While for submerged systems the aeration costs comprise the largest block with over 90 %, their relevance is much lower for side-stream systems (approx. 20 %) (Gander et al., 2000).

In MBR operation, the filtration cycle generally consists of a filtration phase followed by a filtration pause (generally applied for FS membranes) or a backwash (normally applied for HF membranes). The duration and flux during filtration or backwash is mostly selected according to manufacturer’s recommendation or operator’s experience. Nevertheless different filtration modes or feedback controlled fluxes might show better results.

Aeration is used to allow the oxidation and degradation of nutrients in wastewater treatment. Additionally air scouring is applied in MBR to prevent the build-up of filter cake and thus excessive fouling. Especially for submerged systems where aeration accounts for a large part of the total energy costs, optimisation of the hydrodynamics and aeration directly cuts the costs significantly. To achieve higher cross flow velocities and higher shear rates on the membrane surface at a minimal energy input an airlift loop configuration is recommended (Prieske et al., 2008). It is also recommended to operate the system at moderate MLSS levels (to increase the oxygen transfer to the biomass) and low fluxes (Verrecht et al., 2008). While fine bubble aeration is commonly used to aerate the biomass and ensure an optimum oxygen transfer, coarse
bubble aeration is mostly preferred for membrane aeration due to the increased turbulence and shear forces (Judd, 2004). Nevertheless other authors recommend to apply fine bubble aeration (Sofia et al., 2004; Fane et al., 2005).

Wu et al. (2008) evaluated the fouling evolution for different filtration modes. They found that a mixed mode with a high initial flux followed by a period of moderate flux and a backwash yielded the best results. By preventing the SMP (soluble microbial products) to attach directly onto the membrane, keeping the filter cake weakly compressed and reducing the particle accumulation on the membrane the new strategy reduced both the cake and the gel layer. This effect can be explained by particle classification. Drews et al. (2010) conducted a CFD-based theoretical analysis of the drag and lift forces acting on a single particle. They concluded that with lower cross flow velocities larger particles deposited \( (v_{CF} = 0.2 \text{ ms}^{-1} \rightarrow d_{P,crit} \text{ ca. } 3\text{mm}) \) on the membrane than with higher velocities \( (v_{CF} = 0.4 \text{ ms}^{-1} \rightarrow d_{P,crit} \text{ approx. } 0.85\text{mm}) \). Similar effects of particle classification can also be expected during the start-up of the filtration or the change in flux.

Furthermore reactor and module design must be taken into account. Double deck configurations provide twice the membrane area with the same superficial air velocity resulting in a lower specific aeration without influencing the fouling characteristics of each module (Grélot et al., 2009b).

Of course the hydraulic retention time (HRT) and the retention times of the sludge (SRT) or sludge age impact the fouling behaviour. Especially the SRT and consequently the F/M ratio ultimately control biomass characteristics. Higher SRT inevitably leads to higher MLSS concentrations. But it is also thought that the SRT has an impact on microbial products concentration and their fouling propensity as will be discussed in section 2.2.3. Le Clech et al. (2006) assume "that there is an optimal SRT, between the high fouling tendency of very low SRT operation and the high viscosity suspension prevalent for very long SRT". For the design HRT it should be considered that the time is long enough for the microorganisms to decompose the relevant wastewater constituents. Generally it is assumed that unsteady operation conditions can trigger the release of microbial products such as SMP or EPS and thus fouling (Nagaoka et al., 2001; Drews et al., 2006; Le-Clech et al., 2006).

An influence of temperature on permeability is inevitable due to the change in permeate viscosity. Nevertheless, even temperature corrected permeability data often shows seasonal variations. A reason for this can be indirect (and sometimes delayed) temperature effects on the biology, such as release of microbial products or decreased nutrient removal. Kraume et al. (2007) reported that the fouling behaviour of a full-scale plant was strongly related to the concentration of the different nitrogen-components in an MBR. From lab-scale experiments they assumed that the inhibition of nitrite oxidising bacteria is relevant for the permeability (Drews et al., 2007).

### 2.2.3 Biomass characteristics

The three constituents of the mixed liquor – the suspended solids, the colloids and the solute – influence the fouling behaviour of the MBR. While the influence of these has been elaborately evaluated in numerous studies, the results are contradictory.

Bouhabila et al. (2001) studied the influence of suspended solids, colloids and solutes and compared the results to two other studies. While Bouhabila et al. rated the relative impact of the
solute on membrane fouling with 26 %, the other studies (Wisniewski and Grasmick, 1996; Defrance, 1997) came to results of 5 and 52 %.

A literature survey was conducted in order to evaluate the findings on fouling culprits. The result is shown in Table 1. The effects of MLSS, EPS and SMP concentration on fouling are summarised, as well as relevant operation conditions. These constituents of the mixed liquor as well as other sludge characteristics and their impact on fouling will be shortly discussed within the next paragraphs. Furthermore, the operation conditions such as SRT, MLSS, and membrane material and pore size determine what kind of fouling takes place and to what extent.

For the evaluation of the fouling propensity several different set-ups and protocols were used. Generally, one may distinguish between experiments that were carried out under defined conditions within a filtration test cell (here also to be distinguished between dead end or cross flow, unaerated or aerated, constant flux or constant TMP…) and studies evaluating real plant operation data. And even when evaluating real plant operation data, these might be from small lab-plants, pilot plants or full-scale MBR. These differences in scale strongly influence the energy input and hydrodynamics (Kraume et al., 2009) and thus induce different fouling behaviour. Here, also the time-scale plays an important role. While short-term high-flux experiments are thought to trigger particulate fouling, especially long-term low-flux experiments also show irreversible fouling phenomena (Kraume et al., 2009). Flux stepping experiments in test cells and short-term trials can only show trends for full plant operation. While sub-critical fouling is generally thought to be induced by colloids and solutes, suspended solids strongly influence the fouling behaviour for fluxes above the critical flux (Pollice et al., 2005).
<table>
<thead>
<tr>
<th>Study</th>
<th>Effect on fouling</th>
<th>MLSS</th>
<th>EPS</th>
<th>SMP</th>
<th>Pore size</th>
<th>Membrane material</th>
<th>Module</th>
<th>Reactor volume</th>
<th>Duration</th>
<th>SRT [d]</th>
<th>Flux or TMP</th>
<th>TS [gL-1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ahmed (2007)</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td>0.25 µm</td>
<td>Kubota</td>
<td>FS</td>
<td>10 L</td>
<td>20, 40, 60, 100</td>
<td></td>
<td>12.5 Lm⁻¹h⁻¹</td>
<td>5.2-10</td>
</tr>
<tr>
<td>Arabi (2008b)</td>
<td>non</td>
<td></td>
<td></td>
<td></td>
<td>0.047 µm</td>
<td>Zee Weed 1</td>
<td>HF</td>
<td>6.6 L</td>
<td>62 d</td>
<td>15</td>
<td>14 Lm⁻¹h⁻¹</td>
<td>9-10.3</td>
</tr>
<tr>
<td>Bin (2008)</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td>0.22 µm</td>
<td>PVDF</td>
<td>HF</td>
<td>30 L</td>
<td>110 d</td>
<td></td>
<td>1-2.6 Lm⁻¹h⁻¹</td>
<td>start: 6</td>
</tr>
<tr>
<td>Chang (2005)</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td>30000 Da</td>
<td>PES</td>
<td>disc</td>
<td></td>
<td></td>
<td></td>
<td>1.4 bar</td>
<td>0.09-3.7</td>
</tr>
<tr>
<td>Cho (2005)</td>
<td>non</td>
<td></td>
<td></td>
<td></td>
<td>0.2 µm</td>
<td>PES</td>
<td>batch</td>
<td></td>
<td></td>
<td></td>
<td>26-48 Lm⁻¹h⁻¹</td>
<td>9-26</td>
</tr>
<tr>
<td>Drews (2006)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03 µm</td>
<td>PVDF</td>
<td>tubular</td>
<td></td>
<td></td>
<td></td>
<td>60 Lm⁻¹h⁻¹</td>
<td></td>
</tr>
<tr>
<td>Fan (2006)</td>
<td>very little</td>
<td>non</td>
<td></td>
<td></td>
<td>0.1-0.2 µm</td>
<td>PVDF</td>
<td>HF</td>
<td>25-70 L</td>
<td>4 months</td>
<td>8, 15, 40</td>
<td>17.5-20 Lm⁻¹h⁻¹</td>
<td>3.2-8</td>
</tr>
<tr>
<td>Hernández Rojas (2005)</td>
<td>non</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.1 µm</td>
<td>PES</td>
<td>HF</td>
<td>10.5 L</td>
<td>150 d</td>
<td>10, 30, 40</td>
<td>10 Lm⁻¹h⁻¹</td>
<td>5-12</td>
</tr>
<tr>
<td>Jeong (2007)</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td>0.4 µm</td>
<td>PE</td>
<td>FS</td>
<td>12 L</td>
<td>50 d</td>
<td></td>
<td>10 Lm⁻¹h⁻¹</td>
<td></td>
</tr>
<tr>
<td>Kim (2009)</td>
<td>non</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.04 µm</td>
<td>PE</td>
<td>FS</td>
<td>22 L</td>
<td>120 d</td>
<td>10, 20, 40</td>
<td>12 Lm⁻¹h⁻¹</td>
<td>2.5</td>
</tr>
<tr>
<td>Liang (2007)</td>
<td>↑ (short SRT)</td>
<td>non</td>
<td></td>
<td></td>
<td>0.4 µm</td>
<td>Kubota polyolefin</td>
<td>FS</td>
<td>16 L</td>
<td>ca. 260 d</td>
<td>10, 20, 40</td>
<td>26-48 Lm⁻¹h⁻¹</td>
<td>3-7.8</td>
</tr>
<tr>
<td>Meng (2006)</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.1 µm</td>
<td>PE</td>
<td>FS</td>
<td>12 L</td>
<td>4 h</td>
<td></td>
<td>0.04 bar</td>
<td>2-25</td>
</tr>
<tr>
<td>Rosenberger (2002)</td>
<td>non</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.1-0.2 µm</td>
<td>Memcor</td>
<td>UF</td>
<td>Nadir Filtration GmbH</td>
<td>test cell</td>
<td></td>
<td>1 bar</td>
<td>2-24</td>
</tr>
<tr>
<td>Rosenberger (2006)</td>
<td>↑ (short SRT)</td>
<td>non</td>
<td></td>
<td></td>
<td>0.1-0.2 µm</td>
<td>Memcor</td>
<td>UF</td>
<td>Nadir Filtration GmbH</td>
<td>test cell</td>
<td>1 h</td>
<td>1 bar</td>
<td>2-24</td>
</tr>
<tr>
<td>Rosenberger (2005)</td>
<td>non</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.035 µm</td>
<td>Zee Weed 500c</td>
<td>HF</td>
<td>1.5 m³</td>
<td>325 d</td>
<td>2, 3, 4, 5, 10</td>
<td>30 Lm⁻¹h⁻¹</td>
<td>6-10</td>
</tr>
<tr>
<td>Trussell (2006)</td>
<td>↑ (especially at short SRT)</td>
<td></td>
<td></td>
<td></td>
<td>0.035 µm</td>
<td>Zee Weed 500c</td>
<td>HF</td>
<td>1.5 m³</td>
<td>195 d</td>
<td>10, 20, 30</td>
<td>13 or 30 Lm⁻¹h⁻¹</td>
<td>10-28</td>
</tr>
<tr>
<td>Trussell (2007)</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.2 µm</td>
<td>PES</td>
<td>FS</td>
<td>1.44 m³</td>
<td>400 d</td>
<td>10, 20, 40</td>
<td>22 Lm⁻¹h⁻¹</td>
<td>5-28</td>
</tr>
<tr>
<td>Wu (2007)</td>
<td>↑</td>
<td>↑</td>
<td></td>
<td></td>
<td>0.04 µm</td>
<td>Zee Weed 10</td>
<td>HF</td>
<td>227 L</td>
<td>6 month</td>
<td></td>
<td>20-23 Lm⁻¹h⁻¹</td>
<td>4.6-12.6</td>
</tr>
<tr>
<td>Yu (2006)</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
<td>0.1 µm</td>
<td>PE</td>
<td>HF</td>
<td>10 L</td>
<td>6-7 h</td>
<td>40</td>
<td>40 Lm⁻¹h⁻¹</td>
<td>9-10</td>
</tr>
</tbody>
</table>
Influence of MLSS  Suspended solids have been the first suspect for fouling in MBR as they are retained by the membrane and are part of the filter cake. Several researchers evaluated the effects of the mixed liquor suspended solids (MLSS) on filterability. E.g. Rosenberger and Kraume (2002) evaluated the filterability of activated sludge from eight different MBR. While testing mixed liquors from different MBR within a wide range of suspended solids concentration (2 to 24 gL⁻¹) under comparable conditions in a filtration test cell they did not find a correlation with the defined filtration index.

Contradictory to this, Chang and Kim (2005) found a decrease in cake resistance with decreasing MLSS while operating in the low MLSS region (concentrations of 0.09 to 3.7 gL⁻¹).

Also, Meng et al. (2006) found an exponential increase of the filtration resistance with MLSS concentration (2 to 25 gL⁻¹).

Influence of EPS/SMP  Most microorganisms are clustered in the form of flocs or biofilms. The single organisms are thereby embedded in extracellular polymeric substances (EPS). This offers several advantages for the clustered microorganisms, e.g. the establishment of microhabitats (aerobic/anaerobic) within the floc. Additionally, the slimy EPS layer offers some protection against environmental stress (Wolfaardt et al., 1999). EPS consists of several organic macromolecules like proteins, polysaccharides, nucleic acid, lipids and other biopolymers (Frolund et al., 1996) and may be released by the cells or abraded by shearing. In contrast to the bound EPS, this fraction is then considered as the soluble EPS or SMP (Laspidou and Rittmann, 2002) also shown in Figure 2. Typical SMP constituents such as proteins and polysaccharides are also found in wastewater, a differentiation in origin is not possible with surrogate parameters (Drews et al., 2007).

In recent years the constituents of the EPS and/or SMP and especially the polysaccharides have become suspects for membrane fouling and have thus been closely watched. The EPS might fill the gaps within the filter cake (as indicated in Figure 2), leading to a denser and more compact filter cake. Furthermore, the retained polysaccharides might themselves act as a substrate for a biofilm and as a consequence also lead to a dense filter cake (Lesjean et al., 2004).

As usual in the field of membrane fouling, the findings are contradictory. Rosenberger et al. (2006) found a linear correlation between the fouling rate in a pilot MBR and the polysaccharide concentration (in the range of 2 to 15 mgL⁻¹) in the supernatant (SMP fraction). While this trend was unambiguous for a sludge age of 8 d, no trend was observed for a SRT of 15 d. Other authors confirm the importance of SMP or EPS on fouling. Nevertheless, the impact of the different fractions on membrane fouling was evaluated to be different in the different studies. While Kim et al. (2009) found that the protein/carbohydrate ratio in SMP was the most important factor, other authors stressed the importance of the protein concentration in SMP or EPS (Hernandez Rojas et al., 2005; Meng et al., 2006). Own studies showed no correlation between SMP and fouling (Drews et al., 2007; Drews et al., 2008).

From literature it can be seen, that especially the sludge retention time (SRT) seems to play a dominating role for the composition of the activated sludge and the fouling propensity of its constituents. It is generally agreed that the colloids and macromolecules like SMP and especially the carbohydrate fraction of the SMP contribute to fouling to a much larger extent at low SRT (below 20 d). Liang et al. (2007) evaluated the mixed liquor properties at sludge ages of 10, 20 and 40 d. They found increased values for supernatant carbohydrate and protein concentrations.
while the specific UV absorbance, indicating the aromaticity of the SMP decreased for decreasing sludge ages. This correlated to an increased fouling potential at low SRT. Similar observations have been reported by various authors (Rosenberger et al., 2005; Grelier et al., 2006; Liang et al., 2007; Trussell et al., 2007; Dong and Jiang, 2009).

Drews et al. (2008) compared own data with literature values and postulated the thesis that microfiltration (MF) hollow fibre modules are more susceptible to fouling caused by polysaccharides from EPS or SMP than ultrafiltration (UF) flat sheet modules. They argue that the large MF pores can more readily be penetrated by the foulants than UF membranes, thus causing internal fouling. Also HF modules are generally backwashed, thereby removing the filter cake more efficiently than relaxation for FS filtration. While the filter cake causes additional resistance to the filtration, it also acts as a secondary filter layer, saving the membrane from colloidal or soluble foulants.

When discussing SMP and EPS it should always be kept in mind that the sample taking, storage of samples, and analysis might strongly vary for the different studies. While some work groups evaluate the different fractions (especially proteins and carbohydrates), others use sum parameters such as total organic carbon (TOC) or dissolved organic carbon (DOC). An easy to apply staining method was recently described by de la Torre Garcia et al. (2008b). They monitored transparent exopolymer particles (TEP), an acidic fraction of the polysaccharides, for fouling investigations in an MBR. Also advanced techniques like LC-OCD (liquid chromatography with organic carbon detection) or similar to this SEC (size exclusion chromatography) are used to gain information on the molecular weight of the compounds (Lyko et al., 2007; Iversen et al., 2009b). Or the usage of excitation-emission matrix (EEM) fluorescence spectroscopy is applied in order to determine the functional groups of the foulants (Sheng and Yu, 2006; Kimura et al., 2009). Also the extraction methods for EPS might vary strongly. Especially the extraction with exchanger resins and the release by heating are commonly used.

All this influences the results and conclusions (Rosenberger et al., 2005). Although the different analytical methods sometimes correlate to some extent (Rosenberger et al., 2005; Lyko et al., 2008) more often they do not. Therefore values and not even trends can be compared between work groups using different methods.

**Influence of fractal dimension** The fractal dimension df characterises the morphology of a sludge floc. While a higher value refers to spherical and compact aggregates, a lower value indicates loose and linear flocs. From theoretical considerations it can be seen that a low df value is valuable for filtration (Park et al., 2006; Ji et al., 2008) as the porosity of the filter cake decreases with increasing df. The benefit of low df values is also found in practical studies (Meng et al., 2005; Ji et al., 2008). Park et al. (2007) found that the influence of df on porosity is negligible at low df values (indicating a loose and linear floc), while the porosity depended on df for higher values (indicating compact, spherical flocs).

**Influence of particle size distribution** Theoretical models describe the particle deposition and the back-transport from the membrane into the bulk (Elmaleh and Ghaffor, 1996). From the Carman-Kozeny equation it can be seen that the particle size has a strong impact on the hydraulic diameter of the formed channels and thus on the specific resistance of the cake layer.
These results have also been found with spherical polystyrene latex particles (Kwon et al., 2000) and for activated sludge in MBR (Meng et al., 2006; Kim and Nakhla, 2009).

**Influence of viscosity** While the influence of the permeate viscosity and thus the temperature on the filtration performance is obvious from theory, the findings on the influence of the mixed liquor viscosity are contradictory. While Nagaoka et al. (1996) and Meng et al. (2006) found a correlation between the dynamic viscosity of the mixed liquor and the filtration resistance, Rosenberger and Kraume (2002) found none. As reported by Rosenberger (2003) and other authors, sludge is a shear thinning medium. The dynamic viscosity is usually determined using a rotational viscometer. Nevertheless, the shear rate used for characterisation is not always reported in literature. The apparent viscosity of the mixed liquor is strongly influenced by the MLSS content (Rosenberger, 2003). Also the treated wastewater and the microbial structure influence the viscosity.

### 2.2.4 Innovative methods for fouling control

Traditional strategies for fouling prevention mostly try to remedy the effects of fouling by optimisation of hydrodynamics and air scour (Sofia et al., 2004) or operation parameters. Innovative methods including the modification of the membrane by plasma treatment (Yu et al., 2007) or nanocoating (Bae et al., 2006), the electromagnetic deflection of charged coarse particles (Chen et al., 2007), the modification of the suspension by the use of granulated sludge for seeding (Li et al., 2007), the addition of sponge-like carrier particles (Yang et al., 2006a) or granulate (Krause et al., 2008), and flocculation and adsorption have recently emerged. Especially the last approach offers a variety of possibilities and advantages by the addition of tailor-made polymers, natural substances or adapted activated carbons. Nevertheless, systematic studies taking into account not only the effects on filterability, but also potentially negative side effects are rarely reported.
3 Flux enhancers in MBR

3.1 Coagulation, flocculation and adsorption in water and wastewater treatment

Coagulation, flocculation and adsorption are essential processes in water and wastewater treatment especially since the requirements for the elimination of particles and organics in water have stringently increased. Coagulants, flocculants and adsorbents are used in water treatment to remove, e.g., natural organic material (NOM) from water and enhance subsequent filtration (Tomaszewska and Mozia, 2002; Jung et al., 2006; Kim et al., 2006; Kim et al., 2008) or flotation. Furthermore, coagulation and flocculation can be important for the chemical nutrient removal in wastewater treatment (Maurer and Boller, 1999; Wolborska et al., 2006), also in MBR (Song et al., 2008). Chemically enhanced primary treatment is often used in order to reduce the organic load to downstream biological treatment steps, especially in regions with sporadic storm events. This practice reduces high capital and investment costs for biological treatment while allowing rapid start-up and shutdown (Bratby, 2006). The effects, advantages and disadvantages of coagulants, flocculants and adsorbents in MBR will be discussed within this chapter.

3.2 Mechanisms

If not indicated otherwise, the description of the flocculation and coagulation mechanisms are according to Bratby (2006).

3.2.1 Stability and destabilisation

Colloids typically have sizes in the range of 1 nm to 10 µm. They have a very high surface area in relation to their mass. It is thus obvious that the influences of phenomena associated with the surface are predominant to gravity effects caused by their mass. These materials are therefore able to exist as stable dispersions. While direct adsorption or physical straining is possible but complex it might be more interesting to convert these fine particulate, colloidal or dissolved matter into a form whereby separation is more practicable. This can either be done by:

- Changing the surface properties of the particles, thus increasing the adsorptivity of these particles to a given filter medium, or generating a tendency for the formation of larger particles by aggregation.
- Precipitate dissolved material, thus allowing separation by sedimentation or filtration.

By coagulation a stable dispersion or solution can be converted to an unstable system (destabilisation).

Destabilisation and subsequent flocculation is especially interesting for membrane driven separation as most commonly assumed foulants such as SMP (see chapter 2.2.3) are in the size range of solutes and colloids (Nghiem and Schafer, 2006; Rosenberger et al., 2006).

3.2.2 Definitions

Coagulation/Flocculation Although literature on this topic is abundant, a clear definition cannot easily be found. Especially the water treatment industry uses all kinds of definitions of its own, the terms coagulation and flocculation are often being used interchangeably.

According to Bratby (2006), the following differentiations can be made:
• A process whereby the destabilisation of a given suspension or solution is caused can be termed coagulation. Coagulation thus overcomes the factors that guarantee the stability of a system.

• By the term flocculation the process is characterised whereby the destabilised particles come together, make contact and thereby form larger aggregates. Flocculants or filter aids are added to a destabilised suspension and accelerate the formation of flocs and/or strengthen flocs formed during flocculation.

**Adsorption** is the accumulation of atoms or molecules of a gaseous or liquid phase on the surface of a contacting condensed phase. As the atoms on the surface of the adsorbent are not symmetrically surrounded by other adsorbent atoms, adsorbates can fill the missing valence. Depending on the nature of the bonding the process is classified as physisorption if weak van der Waals forces are present or chemisorption if the bonding is similar to chemical bonding (e.g. a covalent bonding) (Schuh, 1981).

### 3.2.3 Rapid Mixing

The section, where a coagulant is added into the liquid to be treated should be rapidly mixed. This stage is thus also termed rapid mixing. According to Bratby (2006) “the rapid mixing stage is possibly the most important operation in the process, since it is here that destabilization reactions occur and where primary floc particles are formed, the characteristics of which markedly influence subsequent flocculation kinetics”. The mixing is mostly characterised by the retention time for this stage and the root mean square velocity gradient G. For metal coagulants G values of 1200 to 2500 s\(^{-1}\) are usually applied in plug flow reactors. The values for polymers are somewhat smaller due to the long chains that should be maintained intact (Bratby, 2006). If the time-scales of destabilization processes are considered, the importance of rapid mixing becomes even more obvious (Bratby, 2006). For water treatment plug-flow in-line reactors are beneficial for most applications (Bratby, 2006). Back-mix reactors (stirred tanks) offer the advantage of adjustable shear gradients for varying flow rates by varying the rotation speed of the impeller. Nevertheless, the shortcoming of these reactors is the broad residence time distribution. In the case of e.g. metal coagulants this can lead to extensive hydrolysis of some of the coagulant (leading to inefficient species) and poor destabilization due to incomplete adsorption or extensive adsorption of metal hydroxide species. Also the dilution of the coagulant influences the mixing characteristics, especially for highly viscous substances. Dilution also impacts on the effectiveness of a coagulant as hydrolysis species might be formed for metal coagulants and the orientation and characteristics of polymer chains depends on the degree of dilution.

In case of sludge treatment or sludge conditioning it must also be kept in mind that high velocity gradients lead to floc breakup, release of SMP, etc. Bratby (2006) thus recommends a laminar flow type reactor. Also the use of baffled chambers or certain static mixers is critical, due to the settling and plugging properties of the activated sludge.

Several different experimental set-ups were used for this work in order to gain a broad set of information on optimum concentration, biotoxicity, formed aggregates and their shear stability and filterability (shown in Table 5). While the additive was dosed into the stirred anoxic chamber of the pilot plant, the mixing conditions where different in the pre-tests (shaking flasks, aerated but unstirred feed tank of the cross flow test cell, etc.). Due to the broad range of
substances and experimental set-ups used within this work the mixing conditions were not
optimized for single substances, but a comparable assessment was conducted. Nevertheless,
differences in small- and pilot-scale might possibly be caused by the different mixing conditions.

3.3 Substances in question

A literature review was conducted in order to find promising additives for fouling reduction in
MBR. In Table 2, respective additives for SMP elimination and flux enhancement are presented.
Activated carbons, metal salts, resins, natural polymers (chitosan or polysaccharide likes),
synthetic polymers (especially cationic as the sludge flocs are usually negatively charged) and
special enzymes might come in question for this task. Some substances have so far only been
used for NOM removal in drinking water or other applications and have not yet been tested in
activated sludge systems. Possible advantages and disadvantages are also listed in Table 2. As
large-scale feasibility and economics are interesting for the low cost treatment of municipal
wastewater, difficult to handle or very expensive substances were excluded from further testing.
Therefore no further investigations were conducted with resins. All other chemicals and also
another very cheap and common biopolymer – starch – were tested within the scope of this work.
In total, 30 different chemicals from the above mentioned categories were investigated.

General aspects of these substances will shortly be discussed in the next paragraphs.

**Powdered activated carbon (PAC)** is produced by carbonisation of carbon rich material such as
wood, coconut shells or crude-oil. Also wood charcoal, lignite or anthracite can be used directly.
The material is activated by chemical or physical (gas) activation (Schuh, 1981). For the physical
activation the precursor is deposited by carbonisation (pyrolysis in inert atmosphere) or
oxidation (exposure to oxidising atmosphere) or a combination of both. For chemical activation
the raw material is impregnated with dehydrating chemicals before carbonisation/activation takes
place. The chemicals must then be extracted by e.g. steam. Nevertheless, residues can cause
problems for later application. The physio-chemical properties (wettability, pore size
distribution, adsorption capacity…) of the activated carbon can be influenced during the
production process. The activated carbon consists of a porous carbon frame with slight mineral
impurities. Due to the random and irregular placement of the crystallites, the activated carbon
possesses a large number of micropores and thus a high surface area and adsorption capacity.
The BET surface (specific surface measured by nitrogen adsorption according to Brunauer-
Emmett-Teller) can be in the range of 500-1500 m²g⁻¹ (Schuh, 1981). Activated carbon is
commonly used for adsorption purposes, such as purification and extraction.

**Metal coagulants** As indicated in Table 2, the metal coagulants can be divided into two groups:
based on iron or based on aluminium. Aluminium or iron based coagulants are quite popular in
water and wastewater treatment due to their availability and their low costs. These coagulants
form multicharged polynuclear complexes in solution, while the nature of the complexes formed
can be controlled by the pH within the system (Bratby, 2006). Characteristics of a product are
the molar ratio of the elements Al or Fe in the solution, the viscosity, the density and the pH.
Most products are available in solid or liquid form and special caution must be taken for storing
these products (stainless or lined steel, glass or adapted plastic tanks).

Also the effects of **calcium and magnesium ions** (naturally occurring in wastewater treatment)
on bioflocculation shall be mentioned here. Arabi and Nakhla (2008a) evaluated the impact of
calcium on membrane fouling. For this, two parallel lab-scale MBRs with synthetic feed were
operated over a period of three months. They found a 35% higher permeability and larger particles for moderate Ca$^{2+}$ influent concentration (280 mgL$^{-1}$), while excessive calcium concentrations (830 mgL$^{-1}$) led to smaller flocs and accelerated fouling. While the SMP removal increased with increasing Ca$^{2+}$ concentration, the excess calcium led to strong scaling. In a second study (Arabi and Nakhla, 2009) they evaluated the ratio of calcium and magnesium on membrane performance. While low ratios showed no improvement, a strong excess of magnesium (Mg/Ca = 5/1) decreased hydrophobic SMP concentration and fouling.

Zhang et al. (2009) found that the resistance of a filter cake formed under high calcium concentration (168.5 mgL$^{-1}$) was distinctly lower than that formed under low Ca$^{2+}$ concentrations (27 mgL$^{-1}$). They also traced this to the flocculation ability of the calcium ions.

Also Kim and Jang (2006) evaluated the impact of calcium concentration (1 and 115 mgL$^{-1}$) on membrane fouling. They found a decrease of filamentous bacteria, better flocculation due to the calcium bridges and less hydrophobic EPS resulting in a reduced fouling rate for higher Ca$^{2+}$ concentrations.

Bratby (2006) also mentions the use of hydrated lime and magnesium carbonate as coagulants for water and wastewater treatment.

**Resins** Ion-exchange resins or ion-exchange polymers are normally provided in the form of small beads, fabricated from an inorganic or organic polymer. The surface comprises a highly developed structure of pores with sites that can trap and release ions. Simultaneously to the trapping of ions other ions from the surface are released, giving this process the name ion-exchange. The resin can be chosen and fabricated according to the needs of the consumer: preference of one or several different types of ions (Schuh, 1981). There are four main types, named after the functional groups: strongly and weakly acidic resins and strongly and weakly basic resins. Resins are used in different separation and purification processes, most commonly in water softening and water purifications where they replaced zeolites to a large extent. While activated carbon is generally used to remove organic contaminants from water, some resins (such as magnetic ion-exchange resins, MIEX) can remove organic ions (Humbert et al., 2005). Also the extraction of EPS from activated sludge is commonly conducted by a resin (Frolund et al., 1996).

**Synthetic polymers** Synthetic polyelectrolytes have “the potential of being applied almost in a tailor-made fashion” (Bratby, 2006), as characteristics like number and type of charged units and the molecular weight can easily be controlled during fabrication. Unfortunately most polyelectrolytes are distributed by producers that keep information concerning the type of polymer, molecular weight, charge density, etc. as a company secret. The consumer therefore has to choose the right product from a range of polymers without the necessary information on the polymer. Often suspension characteristics are varying or not monitored continuously. Effects must therefore be extrapolated from lab trials or evaluated on a trial and error basis.

According to Bratby (2006), the following information would be beneficial for the proper evaluation of a synthetic polymer:

- Type and chemical structure of polymer or copolymer
- Concentration of active ingredient
- Concentration of free monomer
- Concentration and nature of other impurities or constituents
• Molecular weight
• Viscosity under specified conditions
• Proportion of ionisable groups
• Charge density
• Amount of insoluble material present.

Synthetic polymers are available in different forms that can be classified into dry polymers, emulsion polymers and solution polymers (Bratby, 2006). Dry polymers have the advantage of a high active ingredient concentration (80-95 %) and can easily be stored for some time. On the other hand fine and dusty powders can be hazardous in handling and the hygroscopic properties must be considered. Emulsion polymers (25-60 % polymer content) are especially used for polyacrylamide polymers as drying is quite difficult and costly. The micro-sized droplets of polymer and water are suspended in a mineral oil and stabilised by surfactants. While the mineral oil and the surfactants do not improve the performance of the polymer they can severely affect the aquatic environment. As already indicated in the name, solution polymers (10-50 % active polymer, 3-7 % for the more viscous Mannich polymers) contain the polymer dissolved in water. The molecular weights tend to be low, between 5 000 and 200 000 Da, except the Mannich polymers with very high molecular weights. Polymers in this form can easily be further diluted in water. For dry and emulsified products special care should be taken when dissolving the product as the polymers tends to form considerable quantities of gelled solids. A general disadvantage of synthetic polyelectrolytes are contaminants arising from residual unreacted monomers, unreacted chemicals used to produce the monomers and by-products of the polymers in water (Bratby, 2006). Especially the monomers (e.g. acrylamide) can be highly toxic. It is therefore advisable to check the toxicity and approval of the respective authority for any chemical additive before use.

Natural polymers have the advantage of being non-toxic and biodegradable in the environment; nevertheless they are not as widely used as synthetic polymers in water and wastewater treatment. This is probably due to the natural fluctuations in product quality; also synthetic polymers are usually more effective and can be produced to meet special needs of the user. Nevertheless, in certain areas the application can be advantageous as these products are often locally available, while synthetic coagulants might not be. Bratby (2006) mentions the use of different natural polymers that are gained from seeds, starch containing fruits and roots, seaweed or the shells of crustaceans. Some of these substances have been used since ancient times for clarifying water and removing turbidity. Also the use of crushed kernels from cultivated plants like almonds and peaches were then used for this reason in some African countries. Natural polymers are also often used as flocculant aids in conjunction with metal coagulants. This approach reduces the consumption of the environmentally harmful metal coagulant and may lead to cost reductions.

Starches are highly polymerised carbohydrates that can be processed from different natural sources such as potato, corn, manioc, arrowroot and yam. Depending on the processing and substitutions they can be cationic (quaternary ammonium group substitution), anionic (carboxylic substitution) and non-ionic (the natural polymer). Starches are particularly important for the paper production. The molecular weight is in the order of several million Dalton (Bratby, 2006).
Also polysaccharides like guar gums, tannins, chitosan or alginites are used (Bratby, 2006). Chitosan is a cationic biopolymer made from chitin (skeletal substance of crustaceans). The structure of chitin and chitosan is illustrated in Figure 4. The molecular weight is in the range of $10^4$ to $10^6$ Da (Pillai et al., 2009). Its solubility depends on the pH therefore it must be activated with an organic acid (e.g. lactic acid) before use (FranceChitine, 2006). Chitosan has recently been discovered as a flux enhancer for MBR (le Roux et al., 2005; Ji et al., 2008; Koseoglu et al., 2008).

![Figure 4: Structure of chitin and chitosan (Pillai et al., 2009)](image)

**Enzymes** are biocatalysts and accelerate e.g. the numerous reactions of the carbohydrate, protein and lipid metabolism. Enzymes are very selective for their respective substrates. Like all catalysts, enzymes accelerate a reaction by lowering the activation energy. They cannot start a reaction or alter the equilibrium. The catalyst is not consumed during the reaction, thus only a small amount is necessary. Enzymes have been tested for cleaning of fouled membranes in MBR (Brepols et al., 2008; Grélot et al., 2009a), but have proven to be not as effective as chlorine. Nevertheless for sensitive areas they might be an interesting alternative. Different products for membrane cleaning are available (e.g. from Realco and Ecolab). These products were developed mainly for specialized membrane applications in the food processing industry, e.g. fruit juices, beer, wine, dairy/cheese processing or medical application such as blood plasma extraction. They act specifically on e.g. proteins, fats, starch or cellulose. Depending on the used enzyme they might also degrade microbial products such as SMP or EPS (main constituents proteins and polysaccharides) and thus probably trigger flux enhancing effects in MBR.
<table>
<thead>
<tr>
<th>Category</th>
<th>Form/Producer</th>
<th>Removal</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>powder macroporous micro porous</td>
<td>NOM DOM protein humic acids</td>
<td>• possibility of deposit layer • modified structure of biological flocs • removal of toxics • more stable elimination</td>
<td>• deposit layer? • abrasion?</td>
<td>Fang et al. (2006); Ying and Ping (2006); Munz et al. (2007); Lesage et al. (2008); Sagbo et al. (2008); Remy et al. (2009); Satyawali and Balakrishnan (2009)</td>
</tr>
<tr>
<td>Carbohydrate/polsaccharide</td>
<td>starch guar gums</td>
<td>better sedimentation</td>
<td>• natural polymer • cheap • trials for water treatment</td>
<td>• negative impact on the membrane</td>
<td>Campos et al. (Campos et al., 1984a; 1984b) according to Bratby (2006); Koseoglu et al. (2008)</td>
</tr>
<tr>
<td>Chitosan</td>
<td>chitosan salts powder flakes</td>
<td>protein humic acids cells debris</td>
<td>• formation of very large flocs • pH 6-7 • removal of supernatant compounds</td>
<td>• influence of ionic strength • relatively expensive</td>
<td>Bratskaya et al. (2004); le Roux et al. (2005); Meyssami and Kasaeian (2005)</td>
</tr>
<tr>
<td>Enzyme</td>
<td>Lumafast™ Novozymes</td>
<td>protein lipid and other</td>
<td>• pH ≥ 7</td>
<td>• temperature &gt; 35°C</td>
<td>Enzymes as cleaning agents for MBR: Grélot et al. (2009a)</td>
</tr>
<tr>
<td>Metal coagulant</td>
<td>alum polyaluminium chloride (PACl) ferric chloride ferric sulphate heated ferric oxide ferric nitrate etc.</td>
<td>NOM protein humic acids</td>
<td>• possibility of deposit layer • modification of structure of biological flocs • enhanced nutrient removal • removal of supernatant compounds • cheap</td>
<td>• deposit layer? • pH &lt; 7 • disturbance of biological process</td>
<td>Holbrook et al. (2004); Zhang et al. (2004); Jung et al. (2005); Kim et al. (2005); Meyssami and Kasaeian (2005); Wu et al. (2006); Ji et al. (2008); Koseoglu et al. (2008); Song et al. (2008)</td>
</tr>
<tr>
<td>Resin</td>
<td>MIEX (Orica) Dow Chemical Rohn &amp; Haas CER</td>
<td>NOM protein humic acids EPS</td>
<td>• adsorption of components refractory to coagulation &amp; flocculation • pH ~ 7 • successful trials for drinking water</td>
<td>• expensive • no trials for wastewater treatment</td>
<td>Frolund et al. (1996); Bolto et al. (2002); Humbert et al. (2005)</td>
</tr>
<tr>
<td>Synthetic polymer</td>
<td>for ww: cationic SMP TOC</td>
<td>• formation of larger flocs • effects on filter cake • removal of supernatant compounds</td>
<td>• formation of gel layer? • influence of dosage/ionic strength</td>
<td></td>
<td>Yoon and Collins (2006); Hwang et al. (2007); Koseoglu et al. (2008); Thiemig et al. (2008)</td>
</tr>
</tbody>
</table>
4 Evaluation of flux enhancers for MBR

4.1 Literature review: Flux enhancer for MBR

While filtration tests are the most obvious experiments when evaluating possible flux enhancers a set of different experiments might be carried out to gain a thorough understanding of the effects of these additives in MBR. A quick screening is generally conducted by measuring the removal of supernatant compounds by the possible flux enhancers (SMP, TOC, turbidity, etc.). Also the optimum concentration is often determined by these simple jar tests (Shon et al., 2004; Koseoglu et al., 2008; Thiemig et al., 2008). The effects on the mean particle size and/or the particle size distribution (PSD) are also used regularly in order to evaluate or compare flux enhancers (Wu et al., 2006; Ji et al., 2008; Song et al., 2008; Wu and Huang, 2008; Iversen et al., 2009c). As the particle size directly impacts on the filtration resistance (see section 2.2.3) this is a popular parameter. The impact on filterability can either be monitored by test cell trials (generally short-term experiments) or trials within a plant of any scale (lab-, pilot- or full-scale – generally over a longer period). These differences in time and space scales lead to different physical effects as already discussed in section 2.2.3. Main mechanisms and trends can thus be detected, but own studies showed that lab tests generally overestimate the effects of the flux enhancer (Iversen et al., 2009b). The impact of flux enhancers might be somewhat lower in pilot or full-scale plants due to different kind of shear stresses, different mixing conditions the continuous influent, real wastewater constituents and other effects.

The addition of any chemical might lead to unwanted effects within the system. These can include disturbances of the biological system e.g. the oxygen uptake and nutrient removal or accelerated fouling of the membrane due to the added substance itself.

A broad range of studies evaluating the effects of possible flux enhancers under various considerations and conditions is reported in literature. An overview can be found in Table 3. As can be seen, most authors focused on one or very few different additives and only few effects (e.g. SMP removal and/or filterability). The results are usually very promising, but contradicting results are probably not that often published. The results for different categories of flux enhancers are shortly summarised below.

**PAC** influences the fouling behaviour by the adsorption of COD, EPS and other MW fractions (Fang et al., 2006; Ying and Ping, 2006; Akram and Stuckey, 2008; Vyrides and Stuckey, 2009). Li et al. (2005) found that the flocs in mixed liquor spiked with activated carbon were larger and more stable. Satyawali and Balakrishnan (2009) state that the resulting particle size distribution of an activated carbon spiked sludge depends on the ratio of the particle sizes of the PAC and the mixed liquor. According to their theory the resulting particle size is larger if the PAC is larger or of the same size as the sludge flocs. For mixed liquor with a larger floc size as the added PAC the resulting particle size depends on the added concentration. The increase in particle size is attributed to adsorption of organic matter and free bacteria. The microbes can also use the PAC as a support for biofilm growth. The PAC concentration generally applied in MBR is in the range of 0.5 g (Remy et al., 2009) to 2 g (Fang et al., 2006; Satyawali and Balakrishnan, 2009) per litre sludge.

For **metal coagulants** Wu et al. (2006) reported that polymeric coagulants like polymeric ferric sulphate (PFS) had a better effect on filterability than monomeric coagulants. As they can supply more positive charges for organic particles and sludge flocs, charge neutralisation,
removal of supernatant organic matter (measured as total organic carbon in the liquid sample after centrifugation) and floc size enlargement took place more effectively. Also the combination of coagulation (e.g. by FeCl₃) and adsorption (by PAC) is frequently reported (Guo et al., 2005; Haberkamp et al., 2007).

As can be summarised from the different studies the flux enhancing effects of *cationic polymers* can be ascribed to the removal of SMP from the supernatant (Yoon et al., 2005; Hwang et al., 2007; Lee et al., 2007; Koseoglu et al., 2008) the formation of larger flocs (Hwang et al., 2007; Lee et al., 2007; Iversen et al., 2009b; Iversen et al., 2009c) and thus the formation of a more porous filter cake (Hwang et al., 2007; Lee et al., 2007). Generally polymers are found to be very effective for fouling mitigation.

The effects of the natural polymer *chitosan* can mainly be attributed to a strong enlargement of flocs (Tiwari et al., 2005; Ji et al., 2008) and a decreased fractal dimension (Ji et al., 2008). The formed flocs have thus a looser and more linear structure. In addition the increased particle size causes less filtration resistance. Nevertheless, contradicting results were found by Koseoglu et al. (2008). They reported no change in critical flux if chitosan was added to the system but filtration under constant flux was more stable than for the reference.

As can be seen in Table 3, the additive might also improve the permeate quality (Holbrook et al., 2004; Yoon et al., 2005; Lesage et al., 2008). The improvements are generally not striking, but the additive dosing can lead to more stable COD removal or the removal of toxic compounds from the system (Munz et al., 2007; Lesage et al., 2008; Remy et al., 2009), especially in the case of PAC dosing. On the other hand, additives, especially metal coagulants, might cause changes in pH and thus disturb the microorganisms and removal efficiency (Wolborska et al., 2006; Song et al., 2008).

It is mostly recommended to add a flux enhancer before the regular operation starts, i.e. after a main chemical cleaning. If fouling has already taken place, especially during the initial phase of the filtration, the additives are not as effective anymore (Wu et al., 2006). Contrary to this, Yoon et al. (2005) states, “that MPE can restore membrane permeability if it is applied before the cake layer is aged” and an application for peak flow events is recommended.
Table 3: Flux enhancers literature survey

<table>
<thead>
<tr>
<th>Stud</th>
<th>Substance</th>
<th>Main results</th>
<th>Information on operation/s stem</th>
<th>Chronology</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Akram and Stuckey (2008)</td>
<td>PAC</td>
<td>PAC adsorbed high and low MW COD, this was more slowly degraded, thus improved removal performance and flux, adsorbed fine colloids, 1.67 gL⁻¹ are recommended as dosing</td>
<td>Pore size: 0.4 µm, Material: PVDF, Reactor volume: 3 L, Duration: 50 d wo, 60 d with sequential</td>
<td></td>
</tr>
<tr>
<td>2 Fang et al. (2006)</td>
<td>PAC, diatomaceous earth</td>
<td>PAC reduced EPS and thus fouling, inert diatomaceous earth had no effect</td>
<td>Pore size: 0.22 µm, Material: cellulosic, Reactor volume: test cell, Duration: 1.5 h</td>
<td></td>
</tr>
<tr>
<td>3 Guo et al. (2005)</td>
<td>PAC, FeCl₃</td>
<td>Flocculation removed high MW compounds in synthetic ww, flocculation + adsorption whole MW range, Jₜₜ elevated</td>
<td>Pore size: 0.45 µm, Material: PVDF, Reactor volume: test cell, Duration: 4 h</td>
<td></td>
</tr>
<tr>
<td>4 Guo et al. (2008)</td>
<td>MPE 50, PAC, sponge</td>
<td>MPE showed better improvement than sponge addition, P-removal better in sponge system</td>
<td>Pore size: 0.1 µm, Material: PE, Reactor volume: 6 L, Duration: 1 week sequential</td>
<td></td>
</tr>
<tr>
<td>5 Holbrook et al. (2004)</td>
<td>alum</td>
<td>lower TMP, non-settleable concentration, permeate COD, higher floc strength with alum</td>
<td>Material: Zenon, Reactor volume: 11.6 m³, Duration: 16 d, SRT: 25 parallel</td>
<td>sequential</td>
</tr>
<tr>
<td>6 Hwang et al. (2007)</td>
<td>MPE 50</td>
<td>cake layer thicker but more porous, SMP lower but EPS in filtercake higher, larger particles, decelerated fouling in comparison to control</td>
<td>Pore size: 0.4 µm, Material: 1.2 L, Reactor volume: 6 d wo, 10 d with parallel</td>
<td></td>
</tr>
<tr>
<td>7 Ji et al. (2008)</td>
<td>Al₂(SO₄)₃, PFS, Chitosan</td>
<td>PFS best results at 20 Lm⁻²h⁻¹, removal of colloids + solutes, Chitosan best results at 40 Lm⁻²h⁻¹, better flocculation, dₚ increased, dᵢ decreased → larger, looser more linear flocs</td>
<td>Pore size: 0.22 µm, Material: PVDF, Reactor volume: 6 L, Duration: 1.5 month parallel</td>
<td></td>
</tr>
<tr>
<td>8 Kim et al. (2005)</td>
<td>alum</td>
<td>secondary effluent treatment: at low dosage: mainly enlargement of flocs, at high dose also contaminant loading reduction</td>
<td>Pore size: 0.01 µm, Material: PES, Reactor volume: test cell, Duration: 10 h</td>
<td></td>
</tr>
<tr>
<td>9 Koseoglu et al. (2008)</td>
<td>3 polymers, chitosan, starch, FeCl₃, PACI</td>
<td>all very effective for SMP reduction, cationic polymers strongly increase the critical flux and independent of small variations in dosing</td>
<td>Pore size: 0.2 µm, Material: PVDF, Reactor volume: test cell</td>
<td></td>
</tr>
<tr>
<td>Stud</td>
<td>Substance</td>
<td>Main results</td>
<td>Information on operation/s stem</td>
<td></td>
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<tr>
<td>------</td>
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<td>---------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pore size</td>
<td>Material</td>
</tr>
<tr>
<td>10</td>
<td>Lee et al. (2007)</td>
<td>MPE 50</td>
<td>flocs 2.5 times larger, more porous biofilms, soluble COD/EPS were entrapped, increase in bound EPS, enhanced filterability</td>
<td>0.4 µm</td>
</tr>
<tr>
<td>11</td>
<td>Lesage et al. (2008)</td>
<td>PAC</td>
<td>more stable filtration, reduced sludge production, reduced foulants in supernatant, toxic compound (dimethylphenol) adsorbed on PAC and did not influence the biomass</td>
<td>0.2 µm</td>
</tr>
<tr>
<td>12</td>
<td>Li et al. (2005)</td>
<td>PAC</td>
<td>near critical flux 32% higher, air scour more efficient, 1.8 times longer operating intervals, reduced cake resistance</td>
<td>0.2 µm</td>
</tr>
<tr>
<td>13</td>
<td>Munz et al. (2007)</td>
<td>PAC</td>
<td>COD removal higher than estimated with adsorption isotherm → synergetic effects, w/o PAC: inorganic + organic fouling, with PAC: mainly organic and decreased fouling rate</td>
<td>0.4 µm</td>
</tr>
<tr>
<td>14</td>
<td>Qiu (2005)</td>
<td>MPE 50, PAN nanofibers, dissolved chitosan, crosslinked chitosan fibres</td>
<td>biotoxicity tests: no inhibiting effects for additives; idea: insoluble nanofibre → no loss with permeate, dissolved chitosan and MPE effective for turbidity removal and filtration enhancement, fibres not effective</td>
<td>0.4 µm</td>
</tr>
<tr>
<td>15</td>
<td>Remy et al. (2009)</td>
<td>PAC</td>
<td>low PAC dose (0.5 g L⁻¹), higher operation flux possible, less gel deposition on membrane, easier to remove, slightly better permeate quality</td>
<td>0.2 µm</td>
</tr>
<tr>
<td>16</td>
<td>Satyawali and Balakrishnan (2009)</td>
<td>PAC</td>
<td>shock loads possible, high protein/carbohydrate ratio, irregular, less dense cake → slower TMP rise, microbial activity and mean floc size were not altered</td>
<td>30 µm mesh</td>
</tr>
<tr>
<td>17</td>
<td>Song et al. (2008)</td>
<td>alum, FeCl₃</td>
<td>FeCl₃ excluded from further testing due to pH decrease; alum: better P-removal, permeability, larger flocs, pH and N-removal normal</td>
<td>0.4 µm</td>
</tr>
</tbody>
</table>

{23}
<table>
<thead>
<tr>
<th>Stud</th>
<th>Substance</th>
<th>Main results</th>
<th>Information on operation/s stem</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Tiwari et al. (2005)</td>
<td>Chitosan, anionic and cationic part of <em>Sapindus trifoliata</em> seeds upflow anaerobic sludge blanket reactors enlargement of granules, cations more effective, chitosan strongest particle size enhancement, COD removal undisturbed</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>non</td>
</tr>
<tr>
<td>19</td>
<td>Vyrides and Stuckey (2009)</td>
<td>PAC application of PAC for saline sewage in an anaerob MBR: TMP decrease, better DOC removal, SEC showed reduction of high MW compounds, reduction of SMP, reduction of flocs on the membrane</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4 µm</td>
</tr>
<tr>
<td>20</td>
<td>Wu et al. (2006)</td>
<td>Al₂(SO₄)₃, FeCl₃, PACl, PFS polymeric coagulants better than monomeric, higher supernatant organic matter removal, reduced initial TMP and fouling rate, PFS: largest flocs, best filtration results if added before run</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4 µm</td>
</tr>
<tr>
<td>21</td>
<td>Wu and Huang (2008)</td>
<td>PFS PFS removes high MW substances, slower formation of gel layer, enlarges flocs, no severe inorganic fouling</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4 µm</td>
</tr>
<tr>
<td>22</td>
<td>Ying and Ping (2006)</td>
<td>PAC 0, 0.75 and 1.5 gL⁻¹ tested, 0.75 optimal for filtration, PAC forms permeable layer on membrane, rejected COD responsible for fouling; effect: combination of adsorption and scouring</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 µm</td>
</tr>
<tr>
<td>23</td>
<td>Yoon et al. (2005)</td>
<td>MPE 50 reduced SMP, better permeability, less chemical cleaning, MLSS up to 50 gL⁻¹, better permeate quality</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.03 µm</td>
</tr>
<tr>
<td>24</td>
<td>Yoon and Collins (2006)</td>
<td>MPE 50 reduced TMP, better oxygen transfer, lower temperatures were tested, costs savings for membrane and aeration</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>different plants</td>
</tr>
<tr>
<td>25</td>
<td>Zhang et al. (2008)</td>
<td>FeCl₃ reduced SMP with MW &gt; 10 Da and small particles (1-10 µm), bridged negatively charged EPS and replaced other elements by ion exchange, positive effects on TMP evolution</td>
<td>Pore size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2 µm</td>
</tr>
</tbody>
</table>
4.2 Studies conducted within the scope of this work

The effects of possible flux enhancers on filterability, supernatant and mixed liquor characteristics, and the biology have been evaluated in own studies. In total, 30 additives as shown in Table 4 from different chemical categories were tested within the scope of this work. Also the optimum dosage in terms of SMP removal is given in this table. As already shown in Figure 1, the experiments were conducted such that a selection of additives was determined in different pre-studies. These additives were then tested in elaborate long-term pilot trials. The selection scheme, an overview of the used apparatuses, information on the results used for the assessment and resulting publications is given in Table 5. The main outcomes will briefly be presented within the next sections.

It should be noted that it was not possible to conduct all experiments in a short space of time with exactly the same mixed liquor. Due to the broad range of tests carried out for these studies most tests were conducted within two years with the same sludge from the pilot plant described in Iversen et al. (2009b). Nevertheless, the biomass changes due to seasonal variations and unsteady influent concentration etc. might therefore influence the results. Also some of the early pre-studies were conducted with sludge from different systems as the pilot plant was not yet in operation.

Also it should be mentioned that the drinking water in Berlin is very hard (>2.5 mmolCaCO₃L⁻¹) and that the activated sludge therefore has some buffer capacity due to the raw wastewater. In addition, the concentration of humic substances is quite high. The results might therefore be different for plants with different wastewater characteristics.

The membrane material strongly impacts the filtration performance as already discussed in section 2.2.1. Especially parameters like the pore size (distribution), the porosity, surface charge and roughness as well as hydrophilicity or -phobicity influence the membrane fouling behaviour. As flux enhancing additives can change sludge characteristics e.g. the particle size distribution or the zeta potential, the performance of a possible flux enhancer is surely different for different membrane materials. All reported pilot trials were conducted with a PVDF flat sheet membrane module. As can be seen in Table 3 PVDF membranes were also used in most trials reported in literature. Nevertheless, in residual trials with different membrane materials (Iversen et al., 2008) it was found that the effects on membrane of the same material and nominal pore size but from different producers vary strongly. This is surely due to different production methods and subsequent different pore size distribution, porosity and/or roughness of the membrane material.
<table>
<thead>
<tr>
<th>Category</th>
<th>Producer</th>
<th>Product</th>
<th>Further information</th>
<th>Optimum dose $[\text{mgL}^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activated carbon</strong></td>
<td>Norit</td>
<td>SA Super</td>
<td>powder, BET 1150 m$^2$g$^{-1}$</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>PICA</td>
<td>Picahydro LP27</td>
<td>powder, BET 1500 m$^2$g$^{-1}$</td>
<td>5000</td>
</tr>
<tr>
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<td>France Chitine</td>
<td>Chitosan 221</td>
<td>flakes</td>
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</tr>
<tr>
<td></td>
<td>France Chitine</td>
<td>Chitosan 652</td>
<td>powder</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>France Chitine</td>
<td>Chitosan 342</td>
<td>powder</td>
<td>200</td>
</tr>
<tr>
<td><strong>Enzyme</strong></td>
<td>Novozymes</td>
<td>Alcalase 2.5 L</td>
<td>protease</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Novozymes</td>
<td>Viscozyme L</td>
<td>beta-glucanase</td>
<td>*</td>
</tr>
<tr>
<td><strong>Metal coagulant</strong></td>
<td>Merck</td>
<td>FeCl$_3$</td>
<td></td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Ciba</td>
<td>Magnasol 5113</td>
<td>polyaluminium chloride</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>Ciba</td>
<td>Magnasol 5108</td>
<td>polyaluminium chloride</td>
<td>100</td>
</tr>
<tr>
<td><strong>Starch</strong></td>
<td>Rhodia</td>
<td>Rheozan</td>
<td>succinoglucone gummi</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Rhodia</td>
<td>Jaguar C162</td>
<td>guar Gummi</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>Rhodia</td>
<td>Rhopodol 23</td>
<td>xanthan Gummi</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>Tate&amp;Lyle</td>
<td>Mylbond 163</td>
<td>corn starch</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>Tate&amp;Lyle</td>
<td>Mylbond 168</td>
<td>corn starch</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>Tate&amp;Lyle</td>
<td>Mylbond 149</td>
<td>corn starch</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>Roquette</td>
<td>Vector SC 20157</td>
<td>cationic starch</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Roquette</td>
<td>Vector SC 27216</td>
<td>cationic starch</td>
<td>1000</td>
</tr>
<tr>
<td><strong>Synthetic polymer</strong></td>
<td>Ciba</td>
<td>Zetag 7878FS40</td>
<td>cationic polymer, very high MW, high charge</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>Ciba</td>
<td>Zetag 8846FS</td>
<td>cationic polymer, medium MW, high charge</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>Nalco</td>
<td>MPE-50</td>
<td>cationic polymer</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Kurita</td>
<td>M H 260</td>
<td></td>
<td>500</td>
</tr>
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<td></td>
<td>Kurita</td>
<td>MP H 30</td>
<td></td>
<td>500</td>
</tr>
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<td></td>
<td>Kurita</td>
<td>MP 252</td>
<td></td>
<td>500</td>
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<tr>
<td></td>
<td>Kurita</td>
<td>MP L 30</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Adipap</td>
<td>Adifloc KD 450</td>
<td>cationic polymer, very low MW, very high charge</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Adipap</td>
<td>Adifloc KD 451</td>
<td>cationic polymer, low MW, very high charge</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Adipap</td>
<td>Adifloc KD 452</td>
<td>cationic polymer, medium MW, very high charge</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Adipap</td>
<td>Adifloc KD 453</td>
<td>cationic polymer, very high MW, very high charge</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Diagonal</td>
<td>Diafloch CH100</td>
<td>cationic biopolymer</td>
<td>150</td>
</tr>
</tbody>
</table>

* infliction with SMP measurement  ** strongly increased viscosity
Table 5: Selection scheme – assessment of possible flux enhancers

<table>
<thead>
<tr>
<th>Information</th>
<th>Optimum concentration</th>
<th>Biotoxic effects</th>
<th>Particle size, shear stability</th>
<th>Filterability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparatus</td>
<td>shaking flasks</td>
<td>parallel batch tests</td>
<td>rotational viscometer</td>
<td>cross flow filtration test cell</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with additive</td>
<td>without additive</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Air/N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evaluation of</td>
<td>elimination of SMP-PR and SMP-PS</td>
<td>oxygen transfer, respiration, nitrification/denitrification</td>
<td>particle size distribution, shear stability, dewaterability</td>
<td>optimum dosage, additive ↔ membrane interaction, critical flux</td>
</tr>
<tr>
<td>Number of additives tested</td>
<td>30 Selection</td>
<td>13 Selection</td>
<td>12 Selection</td>
<td>7 Selection</td>
</tr>
</tbody>
</table>

Parallel pilot trials with 3 additives (1 starch, 2 syn. polymers)
(Iversen et al., 2009b)
- synthetic polymers very effective, but several promising substances were not tested in pilot
4.2.1 Elimination of supernatant compounds

The elimination of supernatant compounds by flux enhancers has been evaluated in numerous studies (Shon et al., 2004; Koseoglu et al., 2008; Thiemig et al., 2008). As already indicated in chapter 2.2.3, there are various analytical techniques available to analyse supernatant compounds. This should be kept in mind when comparing results from different studies.

For this work, a series of well defined jar tests were conducted. The optimum concentration in terms of SMP-removal was determined for each of the 30 additives (Iversen et al., 2006). Most of the tested substances showed a good to excellent ability to eliminate proteins and polysaccharides from the supernatant. Only some starches and the enzymes caused (due to their chemical composition) an increase in SMP concentration or interfered with the analytical method and were thus excluded from further testing. 13 additives were then chosen for more elaborate studies. The selection was done according to SMP removal efficiency (Iversen et al., 2006; Koseoglu et al., 2008). In addition, at least one chemical component from each category (metal salts, natural and synthetic polymers, activated carbons) was chosen in order to evaluate different physical effects.

![Figure 5: Impacts of additives on SMP removals according to Koseoglu et al. (2008)](image)

Figure 5 shows the SMP removal measured for different dosages of the tested additives. $\Delta c_{\text{SMP}}$ is the difference in SMP concentration of the reference sludge and sludge treated with the respective additive concentration. The samples were taken and analysed after 1 h of shaking. The total SMP concentration was between 86 and 94 mgL$^{-1}$ in the reference; the protein and polysaccharide concentration was 63 to 70 mgL$^{-1}$ and 23 to 24 mgL$^{-1}$, respectively. The SMP concentration was thus quite comparable for all tests. Between 35 and 60 % of the SMP concentration was eliminated at optimum concentration. While several natural and synthetic polymers and the activated carbon showed quite promising results, the
metal coagulants were slightly less effective. For all tested additives an optimum concentration could be found. Surprisingly the concentrations were similar to those found previously with a different sludge (Iversen et al., 2006) shown in Table 4, while no optimum concentration was found in later tests for a sludge with higher MLSS concentration (Iversen et al., 2009b). It can be assumed that for concentrations below the optimum, flocculation or adsorption is limited (due to the limited number of physical or chemical interaction possibilities between the suspension and the additive) causing the lower SMP removal. For higher concentrations deflocculating can take place, due to an excess of charge carriers in the sludge, or other restrictions might lead to no further improvement. All these effects might be influenced by sludge characteristics and ambient conditions such as pH, temperature and MLSS and ions concentration (Mg\(^{2+}\), Ca\(^{2+}\)) (Ernst et al., 2009).

If the addition of a flux enhancer can be controlled by the concentration of fouling causing compounds or the fouling propensity, operation costs and chemicals can be saved. Thus the question occurs what might be the effects of slight over- or underdosing. Here, it was found that metal salts and the biopolymers chitosan and starch are tricky to dose, as over- or underdosing might cause further fouling on the membrane as shown in Figure 6 (Iversen et al., 2007a; Koseoglu et al., 2008). This effect did not occur for the polymers in the tested concentration range. Interestingly, the optimum concentration determined in terms of SMP removal also yielded the best results in terms of filterability (as shown in Figure 6) although the extent of improvement did not correlate with the eliminated amount of SMP (Iversen et al., 2007a; Koseoglu et al., 2008).

4.2.2 Effects on the particle size of the mixed liquor

Kwon et al. (2000) evaluated the effect of different particle sizes on the cross flow microfiltration of monodisperse suspensions of spherical polystyrene latex particles. He found that the critical flux decreased with decreasing particle size. Similar results were also found in real MBR sludge where the filtration resistance increased with decreasing particle size (Meng et al., 2006). By the addition of a flocculant or adsorbent to MBR sludge it is thought to be possible to reduce fouling by forming larger particles or reducing the amount of the very small, colloidal matter.

In own studies 12 different additives (metal salts, chitosans, starches, synthetic polymers and PACs) were tested with regards to their impact on particle size distribution in activated sludge (Iversen et al., 2009c). Table 6 shows the results of these experiments. The grey rows refer to the reference mixed liquor of the respective day. As it was only possible to conduct two to four test series on one day the experiments were carried out on six different days. Mixed liquor was collected freshly before the experiments from the pilot MBR described in (Iversen et al., 2009b). The particle size distribution (PSD) was very similar for all days except the last two when the starches and PACs were surveyed (Iversen et al., 2009c). Nevertheless, only the tested chitosans and polymers were able to significantly increase the volume based particle size (up to 127 %).

As can be seen from the literature, the stability of the formed flocs strongly depends on pH, concentration of the flocculant, molecular weight, charge density and several other system parameters (Bratby, 2006). Especially hydrodynamic forces like shear forces play an
important role in the floc stability (Mühle and Domasch, 1991). For the long-term effectiveness of an additive (especially a flocculant) it is therefore important to know the shear stability of the formed aggregates.

![Graph showing the influence of additive concentration on filterability](image)

**Figure 6: Influence of additive concentration on filterability** (Iversen et al., 2007a; Koseoglu et al., 2008)

Within an MBR system shear forces occur due to pumps, aerators, walls, etc. For sustainable flux enhancement the flocs must therefore be stable in this environment. The dewaterability (capillary suction time – CST) of sheared sludge was measured in order to quickly evaluate the effect of shearing on dewaterability and filterability. Tests were conducted in a range of shear rates dominating in MBR. For most additives, a significant reduction (up to >70 % for several synthetic polymers and chitosan) of the CST was observed. Most additives formed aggregates that were stable in the tested shear range (0-4000 s⁻¹). The polymers caused an approx. 50 % increase in particle size in these lab tests. Nearly no effect of shearing on particle size was observed except for polymer Adifloc KD 452. Here also the CST decreased for the sheared sludge. The increase in mean particle size was only 17-18 % during long-term pilot plant trials. This shows the necessity to evaluate the additives under as real as possible conditions.
Table 6: Effect of additive on CST, apparent dynamic viscosity and medium particle size (v – volume, n – number based) after 5min shearing at 0 and 4000 s⁻¹; changes in comparison to the untreated reference sludge, according to (Iversen et al., 2009c)

<table>
<thead>
<tr>
<th>Shear rate in s⁻¹</th>
<th>CST 0 [s]</th>
<th>Decrease [%]</th>
<th>CST 4000 [s]</th>
<th>4000 [mPas]</th>
<th>d(v 0.5) Increase 0</th>
<th>d(v 0.5) Increase 4000</th>
<th>d(n 0.5) Increase 0</th>
<th>d(n 0.5) Increase 4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>50</td>
<td>51.5</td>
<td>3.18</td>
<td>66.8</td>
<td>66.2</td>
<td>0.628</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td>43.8</td>
<td>12</td>
<td>50.5</td>
<td>3.28</td>
<td>66.9</td>
<td>0.67</td>
<td>0.629</td>
<td>0.2</td>
</tr>
<tr>
<td>PACl Magnasol 5108</td>
<td>40.2</td>
<td>44</td>
<td>2.87</td>
<td>65.5</td>
<td>64.2</td>
<td>0.629</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer MPE 50</td>
<td>10.7</td>
<td>73</td>
<td>12.5</td>
<td>2.9</td>
<td>100.6</td>
<td>96.22</td>
<td>0.616</td>
<td>-2.2</td>
</tr>
<tr>
<td>Ref</td>
<td>39.9</td>
<td>40.7</td>
<td>2.99</td>
<td>63.3</td>
<td>61.5</td>
<td>0.627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chitosan 221</td>
<td>10.6</td>
<td>73</td>
<td>10.6</td>
<td>3.24</td>
<td>143.6</td>
<td>135.8</td>
<td>0.601</td>
<td>-4.4</td>
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<td>Chitosan 652</td>
<td>13.7</td>
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<td>15.4</td>
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<td>78.6</td>
<td>80.2</td>
<td>0.594</td>
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<tr>
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<td>47.1</td>
<td>3.1</td>
<td>63.1</td>
<td>62.4</td>
<td>0.661</td>
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<td>Polymer MPL 30</td>
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<td>43</td>
<td>24.5</td>
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<td>65.4</td>
<td>64.5</td>
<td>0.649</td>
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<tr>
<td>Polymer Adifloc KD 451</td>
<td>11.4</td>
<td>74</td>
<td>12.05</td>
<td>2.86</td>
<td>88.5</td>
<td>84.2</td>
<td>0.627</td>
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</tr>
<tr>
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<td>12.9</td>
<td>70</td>
<td>16.3</td>
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<td>85.3</td>
<td>0.628</td>
<td>-5.3</td>
</tr>
<tr>
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<td>33.3</td>
<td>2.69</td>
<td>64.9</td>
<td>62.5</td>
<td>0.656</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starch Jaguar C162</td>
<td>24.1</td>
<td>28</td>
<td>22.6</td>
<td>2.75</td>
<td>70.1</td>
<td>61</td>
<td>0.688</td>
<td>4.7</td>
</tr>
<tr>
<td>Starch Mylbond 168</td>
<td>26.1</td>
<td>22</td>
<td>23.9</td>
<td>2.74</td>
<td>58.5</td>
<td>57.8</td>
<td>0.712</td>
<td>7.9</td>
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<tr>
<td>Ref</td>
<td>33.1</td>
<td>31.4</td>
<td>2.76</td>
<td>67.7</td>
<td>67</td>
<td>0.821</td>
<td></td>
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<td>PAC SA Super</td>
<td>31.8</td>
<td>4</td>
<td>36.1</td>
<td>2.54</td>
<td>68.5</td>
<td>68.6</td>
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<td>PAC Picahdro LP 27</td>
<td>24.3</td>
<td>27</td>
<td>32.3</td>
<td>2.73</td>
<td>63.2</td>
<td>62.4</td>
<td>0.918</td>
<td>10.6</td>
</tr>
</tbody>
</table>
4.2.3 Filterability trials

In Figure 7, the resistances due to the membrane, internal fouling and the filter cake build-up are depicted. As can be seen, especially the resistance of the filter cake was strongly reduced when a flocculant was added to the mixed liquor (see also (Iversen et al., 2007a)). As shown by Lee et al. (2007) the biofilm architecture, especially the composition and porosity, largely changes if a flocculant is dosed into the system – thus leading to lower resistances. The differences in membrane resistance in Figure 7 can be explained by local differences in the membrane material due to production conditions. This effect was also found by Schipolowski et al. (2006).

![Graph showing resistance during filtration](image)

Figure 7: Resistance during filtration (Rm – membrane resistance, Ri' – resistance due to internal fouling, Rc' – resistance due to filter cake, see also Iversen et al. (2007a))

Also, the so-called critical flux was evaluated for the reference mixed liquor and additive spiked mixed liquor in flux-stepping experiments (Koseoglu et al., 2008). It could be shown that all synthetic polymers (cationic) strongly increased the critical flux by around 40 %. The addition of FeCl3 and PACl both enhanced this value by 14 %. For the natural polymer starch, an improvement of 22 % was found while the addition of chitosan did not change the critical flux. This was astonishing as chitosan strongly reduced the SMP concentration in the supernatant and also showed the strongest effects on the mean particle size as discussed before.

4.2.4 Side effects of flux enhancers in MBR

In residual tests (5 % of the optimum concentration was dissolved in pure water in order to simulate the amount of the chemical that is not bound to the flocs and remains in the liquid phase) carried out in the cross flow filtration test cell it became obvious that especially the tested starch induced strong fouling on all tested membranes (Iversen et al., 2008).

The side effects on the biology and thus on nutrient removal were studied in oxygen uptake and transfer tests as well as nitrification and denitrification tests (Iversen et al., 2008; Iversen et al., 2009a). The tested PACl strongly impacted on nitrification (- 16 %) and denitrification rate (- 43 %). The biodegradable nature of chitosan was striking in endogenous and exogenous tests. Considering the relatively high costs of this additive, an application for municipal wastewater treatment does not seem to be advisable. Also, addition of one of the tested activated carbons strongly impacted on the oxygen uptake rate (- 28 %), nitrification (- 90 %) and denitrification
rate (-43 %), due to a decrease of pH. Results show that the changes in $k_La$ values were mostly insignificant.

### 4.2.5 Long-term evaluation in pilot-scale

From the pre-trials three additives were selected for further testing in the pilot system, the synthetic polymers MPE 50 and KD 452 and the starch Mylbond 168 (Iversen et al., 2009b). While the addition of the chemicals did not change the initial TMP and the evolution during the first 20 - 40 days, the exponential increase and the time when it started were significantly altered.

When a cationic polymer (KD 452 or MPE 50) was added to the activated sludge, a decrease of fouling was observed in comparison to the untreated reference as shown in Figure 8. Especially when KD 452 was added to the sludge the onset of the exponential increase was significantly shifted and came approx. 20 to 30 days later. The initial TMP was easily restored after aeration problems in the polymer spiked plant. Also the fouling rate (as indicated by the slope of the TMP curve) is much lower for the plant with polymer addition. A one week trial with a 30 % higher flux was usually carried out towards the end of each trial period but was not accomplished in the reference plant due to excessive fouling. MPE 50 also showed similarly good results in retarding the fouling. The membrane module producer recommends a main chemical cleaning if the transmembrane pressure exceeds the limit of 0.2 bar. This interval between two main chemical cleaning can thus be prolonged if a flux enhancer is added. The fouling of the MPE 50 spiked plant was less persistent and the membrane permeability was easily restored with a chemical cleaning after the trials, which was not the case for the reference plant (prolonged chlorine contact necessary during cleaning).

A totally different effect was found when the starch Mylbond 168 was added to the sludge. Due to very promising results in the cross flow filtration test cell trials (see Figure 6), Mylbond 168 was selected for further trials in the pilot plant. Nevertheless, the addition had detrimental effects on the membrane. Although (like for the other trials) the initial TMP was around 20 mbar in both plants, the TMP in both plants started to differ significantly after 30 days. After that the
pressure in the starch added plant quickly increased to the limiting value of 200 mbar. This observation also fits with the results from the shaking flask tests where an increase in polysaccharide concentration in the supernatant was found (Iversen et al., 2009b). The starch is not bound to the sludge flocs but penetrates the membrane (“wash out” – a significant COD increase was observed in the permeate immediately after starch dosing) and can cause fouling on the membrane and especially inside the pores.

The contradicting results between the test cell trials and the results from pilot plant operation might be due to the hydrodynamic differences between the test cell and the pilot plant. They further stress the importance to evaluate possible flux enhancers not only by short-term experiments but also in long-term and larger scale trials.

Several characteristic values to describe the mixed liquor, such as SMP and EPS polysaccharides and proteins, biopolymers, CST, particle size distribution and MLSS were also evaluated. While all additives slightly enlarged the sludge flocs, the effects were not as pronounced as expected from the lab tests most probably due to the above described phenomena. Generally the other parameters did not differ significantly between the reference plant and the additive spiked plant during the trials. While these parameters are often analysed and evaluated in hope of finding a universal fouling indicator no striking correlations were observed in this work and other studies (De la Torre Garcia et al., 2009).

It was only possible to evaluate the effect of “wash out” for the tested starch as the high additive concentration caused a significant increase in the permeate COD concentration. The analytical methods to detect the “wash out” of the other tested substances were not available. Nalco confirmed in discussions that they have the possibility to analyse MPE 50 residue in the permeate and have so far not found any permeation effects for the membranes tested. Nevertheless, it is recommended to dose a certain amount per time unit in addition in order to account for additional losses. If the particle size or chain length of the additive and the pore size distribution of the membrane are known the permeation losses can probably be estimated. Otherwise the fate and behaviour of the additives are somehow speculative.
4.2.6 Economic evaluation

The technical assessment showed that the addition of flux enhancers might be an interesting option for the operation of MBR. But for their application in larger scale the question occurs at what expenses these advantages can be achieved in competition with other measures (more surface area, aeration, applied cleaning strategies, etc.). The costs for these additives must therefore be traded off against the savings that can be expected when flux enhancers are used. The following can only be a rough calculation, as the costs and savings depend on several parameters (e.g. the SRT) and the costs for the chemical of course depend on the bought quantity, making it probably more interesting for larger plants.

4.2.6.1 Costs

Before the additional costs due to the chemical addition will be evaluated the treatment costs for MBR treated municipal wastewater will shortly be discussed. The operational costs for the MBR Kaarst-Nordkanal (Erftverband, Germany) are 0.26 € per cubic meter treated wastewater while 0.36 € are reported for the MBR Varsseveld (Water Authority of Hollandse Delta, The Netherlands) by Lesjean at al. (2009). The MBR Kaarst-Nordkanal has 80,000 PE, a maximum dry weather flow of 1024 m³h⁻¹ and a membrane area of 84,480 m² (www.erftverband.de). The MBR Varsseveld is designed for the treatment of 23,150 PE, a flow of 755 m³h⁻¹ and comprises a membrane surface of 20,160 m² (www.mbrvarsseveld.nl). Generally the treatment costs depend on the plant size; they are higher for smaller plants. Taking into account the capital costs, the specific treatment cost of the MBR technology is around 1 €m⁻³ (Lesjean, 2009).

The costs for the additives were determined on the basis of a 10,000 PE MBR with a reactor volume of 833 m³. Naturally the prices vary with the ordered quantity of the substance. As only prices for larger quantities (monthly ordered quantity for the 10,000 PE plant) were asked from the producers the prices might be different for smaller or much larger plants. The price information and additive concentration used for the evaluation can be found in Table 7. It should be noted that the concentration range for the synthetic polymer is quite broad, as different forms (dry and solution polymer) were used. Although PAC concentrations of up to 5000 mgL⁻¹ were used in own studies this concentration does not seem to be reasonable. The evaluated concentration range was therefore set to 450 – 2000 mgL⁻¹, which was similar to concentrations found in literature. As price information was not available for the starch, a range of 0.5 – 10 €kg⁻¹ was assumed. Starch is a natural polymer, widely used in the post processing of paper and it should therefore not be too expensive. But as the starch is often modified this might lead to higher process costs depending on the modification.

Table 7: Additive price information according to producers (September 2009)

<table>
<thead>
<tr>
<th>Category</th>
<th>Additive concentration [mgL⁻¹ mixed liquor]</th>
<th>Additive costs [€kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powdered activated carbon</td>
<td>450 – 2000</td>
<td>1.25 (steam activated) – 3 (chemically activated)</td>
</tr>
<tr>
<td>Starch</td>
<td>300 – 1500</td>
<td>0.5 – 10**</td>
</tr>
<tr>
<td>Synthetic polymer</td>
<td>70 – 500*</td>
<td>2.5 – 6.85</td>
</tr>
<tr>
<td>Metal Coagulant</td>
<td>85 – 100</td>
<td>0.44 – 1.38</td>
</tr>
<tr>
<td>Chitosan</td>
<td>250</td>
<td>15 – 20</td>
</tr>
</tbody>
</table>

*different forms (dry and solution polymer) **estimated price range
Figure 10 shows the additional costs per cubic meter wastewater treated for the different additives according to producers’ information. The re-dosing of the additive was calculated on the basis of the excess sludge withdrawal. The costs thus decrease with increasing sludge age as a smaller amount of additive is taken out of the plant per time unit. Effects such as the loss by biodegradation (as shown for the tested chitosans (Iversen et al., 2009a)) and passage through the membrane, i.e. “wash out” (observed for the starch in our system (Iversen et al., 2009b)) are not considered. Therefore additional dosing might be necessary as also indicated by Thiemig et al. (2008). They re-dosed an additional 16 % per week of a synthetic polymer into an MBR.

Especially polymers are interesting for the application in MBR. As already discussed in the above paragraphs the ones tested improved the filterability while they showed no inhibiting effects on the biomass.

Metal coagulants are exceptionally cheap, but they showed some disadvantages especially on filtration during the pre-tests and were thus not further tested.

As the price for the starch was only estimated and the concentration range is quite broad, the resulting price range is also covering very cheap and quite costly applications. The tested starch showed negative effects on the tested membrane and measuring probes. Nevertheless, as there is a broad range of membrane materials and processed starches, one might find a more promising coupling. Also the price range for the PAC is quite large and the positive impact has been proven in various studies. The price here varies especially due to the kind of activation: the cheaper steam activation or a more expensive chemical activation.

The use of chitosan as a flux enhancer for MBR is pricy. Additional costs of 0.016 to 0.1 € per m³ treated wastewater depending on SRT and charge density (and thus price) were calculated for chitosan. As it is also quite easily biodegradable (Iversen et al., 2009a) additional dosing would be necessary. The use of this additive can therefore be excluded for the treatment of communal wastewater but might be interesting for other MBR applications.

Assuming an additional price of 3 €cent per m³ treated wastewater for a polymer – as these showed promising results in the presented trials – the operation costs would show an increase of approx. 10 % for larger plants like Varsseveld or Nordkanal.

![Figure 10: Cost evaluation for PAC, starch, polymer, metal coagulant and chitosan](image)
The additional operation costs will be even lower if the additive is not dosed continuously but as an emergency action. Nevertheless, this application mode was not evaluated in own studies and will thus not be further discussed.

For the ease of operation solutions are most convenient for dosing. Chitosans and starches are mostly delivered as powders or flakes to avoid biodegradation and reduce transportation costs. They must be dissolved in acids or hot water, avoiding lumps. Also synthetic polymers are sometimes delivered in dry form. Due to the long polymer chains dissolution might be tricky. For the metal coagulants an appropriate storage tank must be supplied in order to avoid corrosion and leakage. For highly viscous chemicals additional mixing might be necessary.

The costs for storing, dissolving, dosing and mixing were not considered here.

### 4.2.6.2 Cost reduction potential

Generally fouling reducing effects are claimed if flux enhancers are applied. Savings can probably arise in conjunction with the membrane cleanings and the installed membrane area.

According to Brepols et al. (2008) the membrane of a MBR can be cleaned physically, chemically or mechanically. A physical cleaning can be conducted by air scour, backwash and/or relaxation of the membrane. A mechanical cleaning can be applied if membrane clogging occurred and the blocking debris is removed. Chemical enhanced backwashes, cleaning in place (CIP – mainly used for maintenance cleanings) or cleaning out of place (COP – usually used for intensive cleanings) are used to chemically clean the membrane. The chemical cleaning methods recommended by the module suppliers are based on a combination of hypochlorite for the removal of organic foulants, and organic acid (often citric acid is used) for the removal of inorganic scalants (Judd, 2006). Due to restrictions in AOX (adsorbable organohalogens) emissions alternatives to chlorine cleanings are frequently being investigated. Nevertheless, these are mostly not very effective and in some cases (e.g. enzymes) quite costly (Brepols et al., 2008; Lesjean et al., 2009). According to Brepols et al. (2008) chemical cleaning agents account for 0.5 to 2 % of the overall operating costs. These relates to approx. 0.2 €m⁻²a⁻¹ (refering to the membrane area). The personnel expenses can only roughly be estimated. Approx. 5 to 20 % of the working time can be connected to cleaning purposes (Brepols, 2009). Larger plants are naturally in the lower cost region. From own trials it can be concluded that a chemical cleaning might be postponed for some time if a polymeric flux enhancer is used. As shown in Figure 8 the operating interval between two chemical cleanings was 40 % longer within the plant with polymer dosing. Therefore, savings in the range of 25 to 50 % can be expected for all costs correlated to chemical cleanings.

Aeration is used for scouring purposes in MBR. If less fouling occurs, or the fouling is less persistent, the aeration can be reduced. Also the oxygen transfer can be improved when certain chemicals are added into the MBR (Yoon and Collins, 2006; Iversen et al., 2009a). The oxygen transfer might be enhanced by changes in e.g. the particle size distribution or the supernatant composition (for example the SMP concentration) as these can impact the surface tension, bubble diameter, viscosity etc. For the already discussed full-scale MBR Kaarst-Nordkanal and Varseveld the total specific energy demand is 0.9 kWhm⁻³. While the total demand is the same, the percental contribution of the aeration (both membrane and bioreactor aeration) is slightly higher in Vasseveld (64 %) than in Kaarst-Nordkanal (59 %). Nevertheless, it is clear that the aeration contributes to a large extent to the operating costs. Measures to reduce the aeration are therefore an important tool to cut costs in MBR operation.
Yoon et al. (2006) estimated the membrane and aeration savings that can be expected by using a synthetic polymer as flux enhancer. As the filtration showed to be stable even at high fluxes, they estimated that flux increases in the range of 50 - 150 % might be possible. The aeration and membrane savings were calculated to be 22 - 40 % and 33 - 60 %, respectively.

Wozniak (2008) estimates that the investment and operation costs can be reduced by 12 % and 18 %, respectively if a flux enhancer is used. The savings in investment can be attributed to less installed membrane area and equipment, while the savings in operation costs are due to lower membrane replacement costs, lower energy consumption and less chemical cleanings.

Own trials showed that a reduction of the membrane area due to the usage of a flux enhancer is not advised. The expected flux and TMP effects might not be as pronounced as for short-term trials. The reported savings are then somewhat lower.

Within the EU funded project AMEDEUS an advanced control system (ACS) was developed (Lesjean et al., 2009). While several input parameters (temperature, pH, flow rates, etc.) are used, output parameters can be the aeration rate, and time and duration for permeate stops or backwashes. First trials showed that it is possible to cut down aeration costs by over 20 % if an advanced control system is installed. One of the input parameters for the advanced control system is the fouling propensity of the sludge which is determined by an online-fouling sensor. Within the project, two fouling sensors were developed: One determining the chemical fouling propensity in terms of SMP content (Mehrez et al., 2007), the other is working on a physical basis (Huyskens et al., 2008). The reversible and irreversible fouling propensity of the mixed liquor is characterised with a mini membrane module. The results are therefore similar to those gained with a filtration test cell that is operated within the MBR (in-situ) (De la Torre Garcia et al., 2008a).

One obvious idea is then to couple the fouling sensor and control unit with a flux enhancer dosing system. The status of the mixed liquor can be monitored and the flux enhancer can be dosed as a conditioner if necessary. Further savings for the maintenance and operation can thus be expected.

![Figure 11: MBR with fouling sensor and controlled flux enhancer dosing](image)

### 4.2.6.3 Patents

If the use of a chemical for flux enhancement is considered it must be respected that there are several patents covering this application. Nalco possesses patents for several countries and the world patent WO2008033703 (Yoon and Collins, 2009). Thereby the addition of cationic polymers with molecular weights greater than 200,000 Da to the activated sludge of an MBR for
industrial wastewater treatment is protected. The reason for the chemical addition can be fouling and foaming reduction, sludge conditioning and flux improvement. Another world patent (WO2003057351) of this company covers the addition of an effective coagulating and flocculating amount of one or more soluble cationic, amphoteric or zwitterionic polymers or combinations of these (Collins et al., 2003). Within another patent the use of at least one high molecular weight water soluble polymer and a method of controlling the polymer dosage, preferably by using fluorescence emission spectroscopy is protected (Shah et al., 2005).

Also the combination of granular activated carbon (GAC) with an MBR is under consideration for patenting WO2009085252 (Conner, 2009). Nevertheless for this application the GAC is only used for pollutant removal and maintained upstream of the membrane.
5 Summary and Conclusion

30 different chemicals were screened w.r.t. their potential for flux enhancement in MBR. Their impact on SMP removal, particle size distribution and fouling propensity of the sludge was considered, but also their biotoxic impact and optimum concentrations were studied. The most promising chemicals were investigated in long-term trials in two identical parallel pilot MBRs (1.6 m³ and 22 m² membrane module each) fed on real municipal sewage. While flocculants were dosed into one system, the other served as a reference. A quick overview of the results is given in Table 8.

Table 8: Selected additives and their positive (+) or negative (-) impact on investigated parameters soluble microbial products (SMP) removal, oxygen transfer coefficient $k_La$, oxygen uptake rate OUR, nitrification/denitrification, particle size (volume based), critical flux $J_{crit}$ and permeability in pilot plant

<table>
<thead>
<tr>
<th>Substance</th>
<th>Supplier</th>
<th>Product</th>
<th>$c_{Add}$ [mgL$^{-1}$]</th>
<th>SMP</th>
<th>$k_La$</th>
<th>OUR</th>
<th>Nitr/deni</th>
<th>Particle size V</th>
<th>$J_{crit}$ test cell</th>
<th>Pilot plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal salt</td>
<td>Ciba</td>
<td>Magnasol</td>
<td>100</td>
<td>+</td>
<td>−</td>
<td>+/−</td>
<td>−</td>
<td>+/−</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Merck</td>
<td>FeCl$_3$</td>
<td>85</td>
<td>+</td>
<td>+/−</td>
<td>+/−</td>
<td>+/−</td>
<td>+/−</td>
<td>+/−</td>
<td></td>
</tr>
<tr>
<td>Chitosan</td>
<td>France</td>
<td>Chitosan</td>
<td>200</td>
<td>++</td>
<td>−</td>
<td>−</td>
<td>+/−</td>
<td>+/−</td>
<td>+/−</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chitin</td>
<td>Chitosan</td>
<td>250</td>
<td>+</td>
<td>+/−</td>
<td>−</td>
<td>+/−</td>
<td>−</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Norit</td>
<td>SA Super</td>
<td>450</td>
<td>+</td>
<td>+/−</td>
<td>+/−</td>
<td>−</td>
<td>+/−</td>
<td>+/−</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pica</td>
<td>Picahydro</td>
<td>5000</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−/−</td>
<td></td>
</tr>
<tr>
<td>Pol mer</td>
<td>Nalco</td>
<td>MPE-50</td>
<td>500</td>
<td>++</td>
<td>+</td>
<td>+/−</td>
<td>−</td>
<td>+/−</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Kurita</td>
<td>MP H 30</td>
<td>500</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kurita</td>
<td>MP L 30</td>
<td>500</td>
<td>+</td>
<td>−</td>
<td>+/−</td>
<td>−</td>
<td>−</td>
<td>+/−</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>Adipap</td>
<td>Adifloc</td>
<td>70</td>
<td>+</td>
<td>+</td>
<td>+/−</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Adipap</td>
<td>Adifloc</td>
<td>70</td>
<td>++</td>
<td>+/−</td>
<td>+/−</td>
<td>−</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KD 452</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starch</td>
<td>Rhodia</td>
<td>Jaguar</td>
<td>300</td>
<td>+</td>
<td>+</td>
<td>−</td>
<td>+/−</td>
<td>−</td>
<td>+/−</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C162</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tate &amp; Lyle</td>
<td>Mylbound</td>
<td>1500</td>
<td>+</td>
<td>+/−</td>
<td>+/−</td>
<td>−</td>
<td>+/−</td>
<td>+</td>
<td>−</td>
</tr>
</tbody>
</table>

++ strong improvement
+ improvement
+/− no effects
− unwanted effects
−− strong unwanted effects

Especially the synthetic polymers showed a high potential as flux enhancers. However, their usage is limited by several patents. Metal salts might be an economic choice but can cause disturbances of the biomass. Also strong dosing effects (over- and underdosing) were observed. When adding a starch to a membrane system it must always be considered that as being a polysaccharide itself it is strongly suspect of causing fouling in the system. This was also observed in the pilot trials. As the starch was not bound to the flocs it permeated the membrane and caused fouling. Nevertheless, today starches can be produced tailor-made to the demands of
the consumer and there are probably couplings of starch and membrane material that show decelerated fouling behaviour. While chitosan strongly reduced the SMP concentration in mixed liquor supernatant and showed the best floc enlargement, the results of cross flow test cell trials showed no improvement of the apparent critical flux. Also the relatively high price of this product limits its application. For a conclusive rating of this substance further tests would be necessary.

Activated carbon has been reported in literature for its positive effects on filtration. While synthetic polymers and starch mainly eliminated large molecular weight substances, the tested activated carbons were able to remove the whole range of molecular weight compounds. For activated carbons the activation method (physically or chemically) should be considered as it strongly influences the price. Also residuals from chemical activation were found to negatively impact the biomass in own trials.

Commonly used shaker or jar tests are an efficient and quick tool to determine the optimum additive concentration. Several parameters such as SMP or TOC removal in supernatant or quick filterability or dewaterability tests can be used for an assessment. Interestingly, the optimum concentration in terms of SMP removal was also found to be the optimum for the cross flow test cell trials in all but one case. Nevertheless, long-term matrix effects can only be evaluated in pilot trials. Own studies showed that the lab-test results overestimate the effects of flux enhancers. Even elaborate test cell trials did not prognosticate the filtration trends within the pilot plant rightly. E.g. the starch showed promising results in test cell trials, but was washed out and accelerated fouling in the pilot plant.

Due to the broad range of tested substances and experimental set-ups used within this work the operating conditions (addition and mixing of the additives, mixed liquor properties such as MLSS concentration, pH, etc.) were not optimized for single substances and varied between the different experiments. Nevertheless, a comparable assessment would otherwise not have been possible. The different results in small- and pilot-scale might possibly be caused by these different conditions. Further research in these fields, especially in effective mixing methods for the activated sludge/additive system in larger scale is necessary.
References


Ji, J., Qiu, J., Wong, F.-s. and Li, Y. (2008): Enhancement of filterability in MBR achieved by


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Appendix: List of Publications

1. Peer Reviewed Journals

5. Kraume, M; Wedi, D; Schaller, J; Iversen, V; Drews, A: Fouling in MBR – What use are lab investigations for full scale operation? Desalination 236 (2009), 94-103.
2. Proceedings


3. Presentations and Posters


* presenting author
Additional to this summary the following publications are part of my thesis:

As first author:

As co-author: