The applicability of the SUR measurement for ultrafiltration of WWTP effluent

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The applicability of the SUR measurement for ultrafiltration of WWTP effluent

Proefschrift

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1 Introduction

1.1 Development of wastewater treatment

There have been a lot of changes in wastewater treatment in the Netherlands since the mid-20th century. In the period 1960 – 1970 governmental and public awareness led to the introduction of the first part of Dutch environmental legislation, the Pollution of Surface Water Act (Wet Verontreiniging Oppervlaktewater, WVO). Here the focus was on the removal of oxygen consuming substances (ammonia and biodegradable organics). Later in the 80s – 90s the objective changed to the removal of nutrients (nitrogen and phosphorus) in order to decrease eutrophication of receiving water bodies. A modern wastewater treatment plant (WWTP) is now able to remove most nutrients up to the parts per million (ppm) level.

Nowadays, new treatment methods and developments to remove heavy metals and organic micro pollutants from WWTP effluent are under investigation. Recently, studies have shown environmental effects linked to the discharge of organic micro pollutants, such as feminisation of male fish and deformation of aquatic animals (Routledge, *et al.*, 1998; Jobling, *et al.,* 2002). In an attempt to counter the unwanted presence of organic micro pollutants in the surface water, the European Water Framework Directive (WFD) was adopted in the year 2000. The WFD aims at a good ecological and biological status for all surface waters, coastal waters, transitional waters and groundwater in Europe by 2015. In total 33 components (nutrients, biological parameters, pesticides, heavy metals, hormone disrupters and medicinal substances) are listed in the WFD as priority compounds. Most likely, it will lead to stricter discharge limits for those 33 priority compounds at WWTPs. In addition to those 33 priority substances, new discharge limits will also be established for 'relevant area-specific' substances (STOWA, 2005).

In addition to the stricter standards the WFD encourages the integration of water reuse[1] options in an integrated approach of water resource management (Bixio and Wintgens, 2006). In this approach WWTP effluent is considered as a water source rather than a waste stream to augment water supply and to decrease the impact of human activities on the environment. In principle, WWTP effluent can be used for any purpose as long as adequate treatment is provided to meet the water quality for the intended use (Asano, 2002). For adequate treatment of WWTP effluent more advanced treatment methods are needed after the biological treatment. Therefore, nowadays the focus in wastewater treatment is changed to advanced treatment techniques to reclaim water from WWTP effluent and to meet future standards. In Table 1.1 an overview of advanced treatment techniques is given according to STOWA (2005).

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[1] In this thesis *water reuse* refers to the use of treated wastewater for beneficial purposes such as agricultural irrigation and industrial cooling, while *wastewater reclamation* refers to the treatment or processing of wastewater to make it reusable. *Reclaimed water* is a treated effluent suitable for an intended water reuse application.

Table 1.1 – Overview of advanced techniques to treat WWTP effluent

Technique	Description
Biological techniques	
Membrane bioreactor (MBR)	An activated sludge system in which the sludge/water separation step takes place via membrane filtration instead of secondary clarifiers.
Advanced nitrogen removal	Removal of nitrogen molecules by nitrification and/or denitrification biomass in the form of a biofilm.
Advanced removal of organic contaminants	Biological removal of organic components by (1) physical/chemical bounding to biomass, (2) active uptake of dissolved organics by biomass and (3) degradation in the cells of biomass.
Pond treatment systems	Man made copies of natural wetland systems to exploit the treating processes (filtration, predation, biological removal nutrients, etc.) that occur in these systems.
Oxidative techniques	
Oxidisation processes	Process to oxidise (complex) organic compounds with the aid of strong oxidants like ozone (O_3) and hydrogen peroxide (H_2O_2).
Advanced oxidisation processes (AOP)	Combination of oxidation processes (O_3 – H_2O_2, O_3 – UV and UV – H_2O_2) that accelerate the oxidation reaction.
Chemical precipitation techniques	
Precipitation	The settling of ionic contaminants from a solution by the addition of chemicals.
Coagulation/Flocculation	The agglomeration of small particles to large flocs, caused by the use of coagulants such as ferric and aluminium chloride.
Coagulation/Flocculation in combination with suspended solids removal	The combination of coagulation, floc-formation and filtration (sand, membrane, etc.) to remove suspended particles and colloidal matter.
Adsorption techniques	
Activated carbon	The bonding of non-polar organic compounds due to Van der Waals forces.
Ion exchange	Bonding of ions to specific charged groups on the surface of a synthetic resin.
Bed filtration	The separation of particles from the water phase, while water flows through the pores in between the filter bed granules. The particles are removed by sieving, adsorption to the filter medium and settling onto the medium.
Screen- and membrane filtration	This type of filtration works by passing water through a filter of a defined pore size. In section 1.3 a more detailed description of this technique is given.
Disinfection	Destruction of micro organisms and the removal of viruses by filtration, physical disinfection (UV) and chemical disinfection (chlorine, ozone and AOP).
Integrated treatment techniques	Techniques that are added to or combined with conventional activated sludge systems like MBR, dosage of powdered activated carbon (PAC) in activated sludge process, etc..

1.2 Reclaiming water from WWTP effluent

Over the past two decades, the amount of municipal wastewater recovered has increased throughout the world (Levine and Asano, 2004). In 2004, Bixio *et al.* reported that worldwide over 3000 (municipal) wastewater reclamation sites existed. Especially in regions of the world faced with water scarcity, WWTP effluent is seen as a potential source for water reclamation. Some examples of water reclamation projects in the world are:

- The Water Factory 21 in Orange County, California (USA) where reclaimed water is recharged into the aquifer in order to stop salt intrusion. The first facility in operation since 1976 consisted of a series of treatment steps: flocculation, multi-media filtration, activated carbon adsorption, reverse osmosis and chlorination. The new facility is called Advanced Water Treatment (AWT) and has been commissioned in 2004. The AWT is designed to produce 325,000 m^3/d of microfiltration filtrate, among which 265,000 m^3/d will be further reclaimed with reverse osmosis. The system may even be expanded in the future to 491,000 m^3/d of product water (Bixio and Wintgens, 2006).
- The WWTP Baix Llobregat in Spain where wastewater is collected and treated from the southern part of Barcelona. Two reclaimed water flows with different qualities are produced at this plant. One for ecological flow, agricultural irrigation and wetlands and a second with a better quality for a barrier against seawater intrusion. The process scheme of the first flow is; regulation basin – flocculation/coagulation – filtration – ultraviolet – disinfection. The water to be used for the barrier against intrusion is additionally treated by microfiltration and reverse osmosis to obtain the required quality (Cazzura, 2008).
- The indirect potable use of WWTP effluent is applied in Wulpen (Belgium). Per year 2,500,000 m^3 WWTP effluent is infiltrated into the dunes after ultrafiltration, reverse osmosis and ultraviolet radiation. The purpose of infiltrating WWTP effluent is to reduce the extraction of natural groundwater for potable water production and hold back the saline intrusion at the coast. After a residence time of one to two months the water is recaptured and used for the production of drinking water (van Houtte and Verbauwhede, 2003).
- In Singapore the NEWater Project was implemented to supply industries and augment freshwater resources with reclaimed water. At the moment 4 water reclamation plants are in operation with a total capacity of about 95,000 m^3/d. The treatment technologies of the water reclamation plants differ, but the core of all the processes are membranes.
- The US $2.0 billion Western Corridor Recycled Water Project (WCRWP) is part of a capital works program of the Queensland Government to secure the future water supply for the region. Treated effluent is collected from WWTPs and further treated at three advanced water treatment plants incorporating microfiltration, reverse osmosis, advanced oxidisation and residual disinfection. The project will supply up to 182,000 m^3/day of purified recycled water for industrial and potable purposes (Traves *et al.*, 2008).
- The only direct potable reuse project is operated in Windhoek (Namibia), one of the driest regions in Southern Africa. About 21,000 m^3/day of water (mixture WWTP effluent and

surface water) is produced per day by a complex treatment chain of coagulation, dual media filtration, ozonation, multi-stage activated carbon adsorption and ultrafiltration prior to chlorine disinfection (Menge *et al.*, 2007).

- The DECO plant of Evides Industriewater (supplier of industrial water), in the southwest of the Netherlands (Zeeuws-Vlaanderen). This plant has been in operation since the year 2000 and produces an aggregate of 750 m^3/h demineralised water, 750 m^3/h cooling tower supply water and 1200 m^3/h ultra-pure water for the Dow Chemical Company. Part of the demineralised water is produced from effluent of a local communal WWTP in the vicinity of the plant. The applied technologies to upgrade the WWTP effluent to demineralised water are microfiltration followed by reverse osmosis; the design capacity is 2.2 million m^3/year (van Agtmaal *et al.*, 2007).

Considering the given examples it is clear that wastewater can be reused for various purposes including a whole range of less advanced to more highly advanced purposes. The primary incentives for implementing water reuse were augmentation of water supplies and/or pollution abatement (Levine and Asano, 2004). Nowadays on an international scale, direct non-potable water reuse is currently the dominant mode for agricultural irrigation, industrial cooling water, river flow augmentation and other applications. In Table 1.2 a summary of the various possible applications from a global perspective is given.

Table 1.2 – Categories and description of water reuse applications from a global perspective according to Asano (2002)

Category	Description
Agricultural irrigation	Use of reclaimed water restricted to agricultural purposes and worldwide the largest current use.
Landscape irrigation	The second largest user of reclaimed water in industrialised countries and it includes the irrigation of parks, playgrounds, golf courses, etc.
Industrial reuse	The third major use of reclaimed water for a diversity of industries including power plants, pulp and paper and other industries with high rates of water utilisation.
Groundwater recharge	Include groundwater replenishment by assimilation and storage of reclaimed water in groundwater aquifers and the establishment of hydraulic barriers against saltwater intrusion in coastal areas.
Environmental and recreational uses	Involve non-potable uses related to land based water features such as the development of recreational lakes, marsh enhancement and stream flow augmentation.
Non-potable urban uses	Use of reclaimed water for fire protection, air conditioning, toilet flushing, construction water, flushing sanitary sewers, etc.
Indirect or direct potable reuse	Potable reuse occurs either by blending in water supply storage reservoirs or by the direct input of reclaimed water into the water distribution system.

1.3 Membrane filtration

1.3.1 Ultrafiltration membranes

Membrane filtration is a treatment process based on the physical separation of compounds from the water phase with the use of a semi-permeable barrier (membrane). Membranes for water treatment are pressure driven and can be divided into two categories based on their sieving mechanism (Mulder, 1996): porous and dense membranes. Porous membranes processes are microfiltration and ultrafiltration and their separation mechanism is sieving achieved by the pore size. The distinction between microfiltration and ultrafiltration is based on the size of the pores. Microfiltration features pore sizes of 100 nanometer (nm) up to a few micrometers (µm) while the ultrafiltration membranes feature smaller pores, from 1 – 100 nm. At lower pore size of the ultrafiltration membranes the charge of the membranes might be active as a separation mechanism as well. Nanofiltration and reverse osmosis are dense membranes that are able to retain dissolved salts and solids from water. By nanofiltration low molecular weight components and divalent ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, CO_3^{2-}, etc.) can be separated and furthermore monovalent ions (Na^+, K^+, Cl^-, NO_3^-, etc.) can be rejected by reverse osmosis. The driving force for porous and dense membrane processes in water treatment is usually a hydraulic trans membrane pressure (TMP). It is obvious that the operating TMP of dense membranes is much higher than that of porous membranes. Table 1.3 outlines the typical pore sizes, required operational TMP and removable components of the different membrane processes for water treatment. It is mentioned that the pore size range related to each of the membrane processes is not fixed: slight variations can be found in the literature.

Table 1.3 – Classification of membrane processes with the pore size, pressure and removable components for water treatment (Mulder, 1996)

Membrane process	Pore size (nm)	Pressure (bar)	Removable component
Microfiltration	100 – 1000	0.1 – 2	Suspended solids, bacteria
Ultrafiltration	10 – 100	0.1 – 2	Macromolecules, viruses, proteins
Nanofiltration	1 – 10	4 – 20	Micropollutants, bivalent ions
Reverse osmosis	0.1 – 10	10 – 30	Monovalent ions, hardness

Many WWTP effluent reclamation plants rely heavily on membranes. Bixio and Wintgens (2006) state that the combination of microfiltration/ultrafiltration and reverse osmosis is the most applied scheme for the production of high quality water. Reverse osmosis itself has been used for desalination of WWTP effluent already since 1970 but the combination of microfiltration/ultrafiltration and reverse osmosis (double membrane system) has been developed recently. Initially pretreatment of reverse osmosis had been based on technologies like flocculation, lime clarification, recarbonation, settling and filtration. Compared to these pretreatment technologies microfiltration and ultrafiltration are superior in removing suspended solids, bacteria, large macro-molecules and pathogenic organisms, in order to provide a high quality feedwater to the reverse osmosis system. Although microfiltration and ultrafiltration are operated under similar process conditions, they differ in pore size characteristics (see Table 1.3). Ultrafiltration membranes are able to reject viruses completely where microfiltration does not. Also in the combination with reverse osmosis membrane differences are found. Kim *et al.*, (2002) present lower operating pressures and longer cleaning intervals when reverse osmosis membranes are fed with ultrafiltration filtrate instead of microfiltration filtrate.

The research described in this thesis focuses on the ultrafiltration membranes because of their good references. The ultrafiltration membranes have a proven capability to produce a stable and good filtrate quality in terms of particles and microbial parameters, regardless of the feedwater quality. Beside this the ultrafiltration membranes are able to operate at relatively high flux, low TMP and low energy costs, applying dead-end mode (te Poele, 2005).

1.3.2 Membrane process

In a membrane process three different streams can be defined (Figure 1.1). First the feed stream containing the constituents that have to be removed. The feed stream is split into two streams by the membrane; a clean water stream (the permeate) and the stream containing the retained constituents (the concentrate). The separation is mostly forced by pressure in water treatment, the so-called (hydraulic) trans membrane pressure. Depending on the height of the TMP and the filtration resistance water will flow from the feed side through the membrane to the permeate side with a certain flow rate called the flux (J).

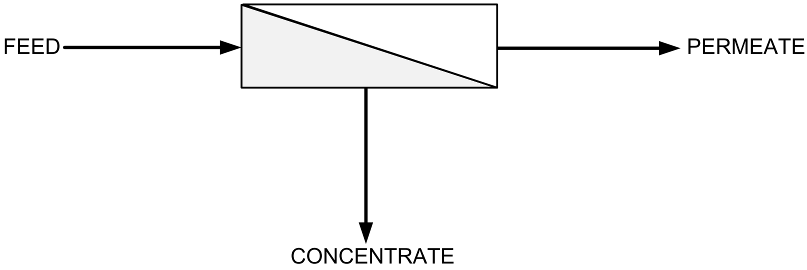

Figure 1.1 – Schematic representation of a membrane process

The membrane process can be designed in different ways. Generally three main aspects should be considered during the design of the membrane process: the membrane material, membrane configuration and mode of operation. These aspects will be described and discussed in the following section.

1.3.3 Membrane material

Membranes are made of various organic and inorganic materials. The most commonly applied in water treatment are the organic membranes with a wide variety of membrane materials, pore size, pore size distributions, membrane configurations and production processes. Compared to the organic membranes, inorganic membranes have superior mechanical strength and resistance to chemicals and temperature but the manufacturing costs are much higher. Although the prices of ceramic membranes are decreasing and therefore they are becoming more and more attractive (Baker, 2004) and will compete with organic membranes.

Formerly the organic membranes were made of cellulose, a natural material but nowadays most of the ultrafiltration membranes are mainly made of polymers with hydrophilic properties like polysulfone, polyethersulfone or polyvinylidene fluoride (Meier *et al.*, 2006). In Table 1.4 the different membrane materials are summarized. The membrane structure can be isotropic or anisotropic. Whereas isotropic membranes have a uniform composition and structure, anisotropic (or asymmetric) membranes consist of different layers, prepared by a phase inversion process, each with different structures and permeability (Baker, 2004).

Table 1.4 – Different membrane materials (Mulder, 1996)

Organic		Inorganic	
Cellulose acetate	(CA)	*Ceramic*	
Polyetherimide	(Ultem)	Titanium Oxide	(TiO_2)
Polyacrylonitrile	(PAN)	Zircon Oxide	(ZrO_2)
Polysulphone	(PSU)	*Metallic*	
Polyethersulphone	(PES)	Aluminium Oxide	y-Al_2O_3
Teflon			
Polyvinylidenefluoride	(PVDF)		
Polyethylene	(PE)		

1.3.4 Configuration

The configuration of membranes generally differs in two ways based on their geometry: as flat sheet or tubular. The application of one of the configurations mainly depends on the feedwater characteristics. An ideal configuration would provide a high membrane area per volume area (packing density), high turbulence, low energy use, easy cleaning and operation. However, some of these features are conflicting and therefore result in a number of configurations in terms of membranes and membrane module. The two geometries and different features form the basis for four principle types of membrane modules used for wastewater treatment (Aptel and Buckley, 1996; Mulder, 1996):

- Tubular membranes; having an internal diameter larger than 3 mm and packing density of < 300 m^2/m^3, which are bundled in a module.
- Hollow fibre or capillary membranes; having an internal diameter less than 3 mm, which are bundled into a membrane module with some hundred or thousand fibres. The difference between hollow fibre and capillary membranes lies in the packing density, which is about 600 – 1200 m^2/m^3 and values of 30,000 m^2/m^3 respectively (te Poele, 2005).
- Plate or frame membranes; comprised of a series of flat sheet membranes and support layers and having a packing density of 100 – 400 m^2/m^3.
- Spiral wound membranes; flat membranes wound around a spacer, having a packing density of 300 – 1000 m^2/m^3 and used for nanofiltration and reverse osmosis.

In tubular and hollow fibre membranes the flow direction of feedwater can be inside-out or outside-in. During outside-in filtration permeate is collected inside the membrane and during inside-out it is collected outside the membrane fibre. This is illustrated in Figure 1.2.

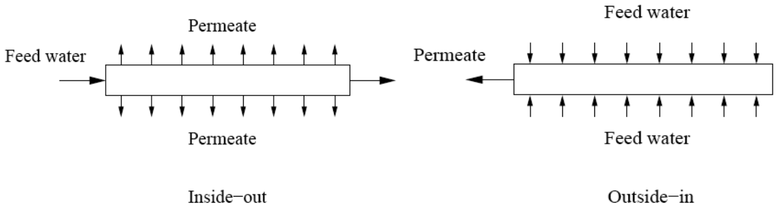

Figure 1.2 – Schematic representation of inside-out and outside-in filtration (te Poele, 2005)

1.3.5 Modes of operation

Membrane filtration can be operated basically in two modes: dead-end and cross-flow operation, illustrated in Figure 1.3. In the early days of membrane filtration with ultra- and microfiltration membranes, cross-flow filtration was the only applied mode of operation (van de Ven, 2008). In cross-flow filtration the feed flow is tangential to the membrane surface at a high speed. The aim of this high speed is to prevent the deposition of material of the feed solution on the membrane surface. During dead-end ultrafiltration all the deposits of the feed solution accumulate on the membrane surface and lead to an increase of pressure when the permeate flow is kept constant. Therefore, cross-flow filtration is more suitable for treating water with high solids content and higher permeate production can be achieved. However, the required velocity of cross-flow filtration leads to a high energy usage. To overcome the disadvantages of both modes of operations recently an intermediate mode of operation has been introduced: semi dead-end operation. In this mode the membrane is dead-end operated but accumulated deposits are frequently removed by hydraulic flushes. This type of operation is becoming an attractive filtration mode for WWTP effluent and is also applied during the research described in this thesis.

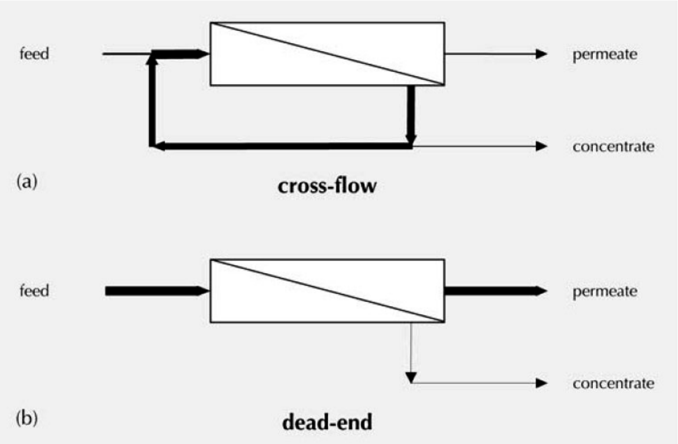

Figure 1.3 – Schematic representation of cross-flow filtration (a) and dead-end filtration (b) (Roorda, 2004)

In order to maintain stable operation during semi dead-end operation the membranes should be cleaned periodically. Cleaning can be performed either hydraulically, mechanically, chemically or by electrical cleaning. Hydraulic cleaning can be applied in two flow directions. A forward flush is a complete cross-flow cleaning method with high flow rates. With a backflush the flow rate is changed in the opposite direction, which means that backflush water is flowing from the permeate side to the feed side of the membrane and is discharged as concentrate.

After several filtration periods the performance declines, in spite of frequently applied hydraulic flushes. Chemical cleaning is needed to recover the performance of the membrane. This cleaning method can be applied by either starting with a forward or a back flush. Subsequently the membranes are soaked in chemicals for a certain period and finally the membranes are flushed with permeate, tap water or ultra pure water.

1.4 Ultrafiltration definitions

1.4.1 Flux and resistance

During ultrafiltration the TMP is the driving force for permeation. The permeate flow through the membrane is called flux (J) and is defined as the permeate volume through the membrane per unit of membrane area. The permeate flux is expressed as $m^3/m^2 \cdot s$ or more commonly $L/m^2 \cdot h$ and is given by the Equation 1.1 (Mulder, 1996).

$$J = \frac{dV}{dt} \cdot \frac{1}{A_{membrane}} \tag{1.1}$$

in which:
J = flux ($m^3/m^2 \cdot s$), in this thesis expressed as ($L/m^2 \cdot h$)
V = filtered volume (m^3)
t = time (s)
$A_{membrane}$ = membrane area (m^2)

The relation between the permeate flux and the trans membrane pressure under laminar conditions and through porous membranes can be described conveniently by an adaptation of the Darcy's law (Lojikine *et al.*, 1992) and is introduced in Equation 1.2.

$$J = \frac{\Delta P}{\eta_p \cdot R_t} \tag{1.2}$$

in which: ΔP = trans membrane pressure (Pa), in this thesis expressed as (bar)
η_p = dynamic viscosity of the permeate (Pa·s)
R_t = total resistance to filtration resistance (m^{-1})

Equation 1.2 presents an inversely proportional relation between the permeate flux and the dynamic viscosity. In water and wastewater treatment it is usual to assume permeate viscosity equal to pure water (Manem and Sanderson, 1996) and therefore solely dependent on its temperature. In the literature several empirical relationships between temperature and pure water viscosity can be found; in this thesis the one as derived by Janssen and Warmoeskerken (1997) is used and shown in Equation 1.3.

$$\eta_p = 10^{-3} \cdot \exp^{0.580 - 2.520\theta + 0.909\theta^2 - 0.264\theta^3} \tag{1.3}$$

in which: θ = empirical factor: 3.6610·(T/(273.1+T))
T = temperature (°C)

When the object of filtration is not pure water (i.e. WWTP effluent) a contribution to the resistance may arise from the solute and other substances, which cause fouling (thoroughly described in chapter 2). Therefore the total filtration resistance (R_{total}) is often expressed as the sum of membrane resistance ($R_{membrane}$) and the additional resistance from fouling ($R_{fouling}$) as presented in Equation 1.4.

$$R_{total} = R_{membrane} + R_{fouling} \tag{1.4}$$

1.4.2 Filterability and reversibility

Dead-end ultrafiltration operation consists of subsequent filtration, backflush and chemical cleaning steps. The definitions of the various cycles are used throughout this thesis, as well as the definitions of *filterability* and *reversibility* used in this work are graphically given in Figure 1.4. Filterability is the increase of filtration resistance over time (or filtrated volume). A good filterability means that the increase of resistance is small. Reversibility is described as the extent to which the filtration resistance is returned to the original value after applying a hydraulic cleaning. If the filtration resistance after a backflush is equal to the filtration resistance at the start of the previous filtration period, than the fouling is considered to be completely reversible. Both terms, filterability and reversibility are related to the properties of the feedwater, membrane material and operational conditions. Therefore, the definitions are used in respect to these parameters. When the amount of irreversible fouling becomes too high, or after a predetermined amount of backflush cycles, the membrane is chemically cleaned. Ideally, chemical cleaning removes all the irreversible fouling from the membrane.

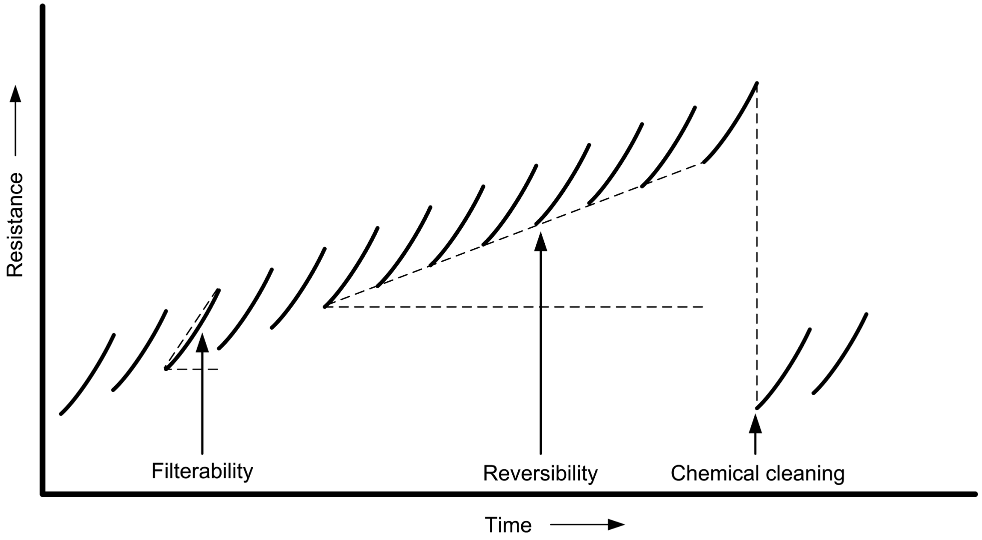

Figure 1.4 – Typical filtration curves illustrating filterability, reversibility and chemical cleaning

1.5 Background of this thesis

Since 1999 research at Delft University of Technology has been carried out on dead-end ultrafiltration of WWTP effluent. From 1999 – 2005 the research was performed in the framework of the project “Membrane filtration of effluent”. The overall objective of the project was to develop filtration techniques for the large-scale distribution of reclaimed water, based on biologically treated effluent. Within the project the researchers focused on dead-end ultrafiltration. The aim of this part of the project was to gain more insight into the interaction between WWTP effluent and the ultrafiltration membranes in order to improve the design of ultrafiltration installations at lower costs.

The research at the Delft University of Technology has resulted until now in two dissertations. The first dissertation ‘Filtration characteristics in dead-end ultrafiltration of WWTP effluent’ published by Roorda (2004) deals with the filterability of WWTP effluent. In addition to pilot experiments at various WWTPs in the Netherlands the filterability of WWTP effluent was studied in detail on lab scale. These experiments resulted in a new parameter to describe the filtration characteristics of WWTP effluent during dead-end ultrafiltration, the Specific Ultrafiltration Resistance (SUR). With the SUR it is possible to measure even small differences in filtration characteristics of WWTP effluent (Roorda, 2004). The SUR was also used to measure the filterability of size fractions of the WWTP effluent. In chapter 3 the SUR equipment and measurement are described in detail.

The second dissertation deals with the physical and chemical mechanisms of membrane fouling during dead-end ultrafiltration of WWTP effluent (te Poele, 2005). To gain insight into this matter, photometric measurement methods are further developed in order to analyse potential membrane foulants in WWTP effluent. The analytical data of the foulants are compared with the actual filtration properties of WWTP effluent on lab and pilot scale. More details about the membrane foulants in WWP effluent were obtained by using different cleaning agents and methods in laboratory and pilot filtration tests. In chapter 2 the results of this dissertation are discussed in more detail.

In 2005 the research project was continued under the name "Ultrafiltration of WWTP effluent". This research focuses on the application of ultrafiltration of WWTP effluent for high quality industrial applications. Within the project two research topics were defined. The first topic deals with the improvement of filterability of WWTP effluent by pretreatment before ultrafiltration. Roorda (2004) stated earlier that an high initial filterability of WWTP effluent is required for stable ultrafiltration performance at fluxes as high as 100 $L/m^2 \cdot h$ and also showed that the filterability is dominated by particles in the range of 0.1 – 0.2 µm. Therefore for a high initial filterability of WWTP effluent particles in this particular size range should be removed or transformed during pretreatment for ultrafiltration. Pilot and lab scale experiments showed that with conventional pretreatment techniques (coagulation, sandfiltration and double layer filtration) only a moderate improvement of the initial filterability could be obtained. Therefore within this topic the application of alternative pretreatment technologies is investigated. The second topic deals with the SUR measurement and the operation of ultrafiltration installations. In this part the filterability of WWTP effluent measured as the SUR value and the performance of UF installations are evaluated. It is well known that the performance of UF installations depends on the filtration characteristics of the effluent. But this relation is not yet really quantified and therefore this part of the research focuses on the relation between SUR and process parameters like flux, trans membrane pressure and resistance increase.

1.6 Aim of this thesis

The research described in this thesis deals with the filterability and reversibility of WWTP effluent during dead-end ultrafiltration in order to optimise the process conditions and pretreatment technology of dead-end ultrafiltration. To gain insight into this matter, the following aspects are covered:

- Investigation of the relation between the SUR value of WWTP effluent and operating flux, trans membrane pressure and resistance.
- Identification of the effect of four pretreatment technologies: powdered activated carbon, granulated activated carbon filtration, dual media filtration and biological granulated

activated carbon filtration (1-STEP® filter). The effect is determined by fractionation, foulants and SUR measurements of untreated and pretreated WWTP effluent.

- Evaluation of the performance of a pretreatment technology (coagulation – dual media filter – coagulation) and full scale ultrafitration installation during the intake of WWTP effluent after buffering in a stabilization pond. For the evaluation SUR measurements and foulants analyses are performed.
- The effect of operational conditions flux and pretreatment on both fouling parameters, filterability and reversibility. To determine this effect a pilot ultrafiltration installation is used.
- Characterization of both filterability and reversibility of WWTP effluent with a revised version of the SUR equipment.

With the gained insight it should be possible to further implement or optimize the application of dead-end ultrafiltration of WWTP effluent at different locations and in different situations in order to increase the perspectives of water reuse for different applications.

1.7 Outline

For a general understanding of the terms and concepts in membrane filtration of WWTP effluent a concise introduction is presented in *Chapter 2 WWTP effluent and membrane filtration. Chapter 3 Research methodology* describes the material and methods used during the experiments. *Chapters 4 – 7*, the heart of the thesis, present the results of the experiments. *Chapter 4 Filtration properties and performance of ultrafiltration installations.*presents the results of tests at the WWTP Sas van Gent (full scale) and WWTP Horstermeer (pilot scale) to investigate the relation between the SUR value of WWTP effluent, flux, trans membrane pressure and resistance increase. *Chapter 5, Filtration properties and pretreatment*, focuses on the effect of powdered activated carbon, granulated activated carbon filtration, dual media filtration and biological granulated activated carbon filtration (1-STEP® filter) on the filterability of WWTP effluent. The next chapter, *Application of SUR in practice: A case study*, presents the added value of applying SUR measurements parallel to the operation of a full scale ultrafiltration – reverse osmosis installation. The effect of operation conditions on both filterability and reversibility are presented in *Chapter 7*. Finally in *Chapter 8* the results of the various experiments are evaluated and several recommendations for future research directions are proposed.

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2 Wastewater treatment plant effluent and membrane filtration

2.1 Introduction

This chapter provides the background information for this thesis. In section 2.2 the municipal wastewater treatment process and the characteristics of WWTP effluent are described. Further in section 2.3 the fundamentals of membrane filtration for water treatment are addressed and in section 2.4 the main drawback of this process: fouling. The subsequent sections provide information about factors that affect this almost inevitable consequence of membrane filtration. The last section gives an overview of methods to indicate the fouling rate of WWTP effluent.

2.2 Wastewater treatment plant effluent

2.2.1 Treatment process

Nowadays in the Netherlands almost all the produced municipal and industrial wastewater (>98%) is treated in wastewater treatment plants (CBS, 2006). The municipal wastewater treatment plants (356 in 2007) with a total design capacity of 24,462,000 population equivalents (pe's) and a total volume of wastewater treated of approximately 2,100 Mm^3 in 2007 (CBS, 2009). In general almost all the current wastewater treatment plants in the Netherlands are based on the activated sludge process (Figure 2.1). Therefore the description of the treatment process in this section focuses on this process. The activated sludge process consists of three processes in series. The first step, the primary treatment, is usually mechanical aiming to remove coarse material, suspended solids and other undesired substances. Subsequently, in the second step, the "heart" of the process, the influent is mixed with biomass (activated sludge) and treated under aerobic and/or anoxic conditions. These conditions provide not only a removal of biodegradable COD but also a conversion of phosphorus and nitrogen. In the end the biologically treated water and the activated sludge are separated in a final clarifier using gravitational settling. The settled activated sludge is returned partly to the beginning of the biological process and the other part is wasted. In many cases the wasted sludge is treated on site together with the sludge of the primary step by digestion and dewatering. After dewatering it is usually transported to an incinerator.

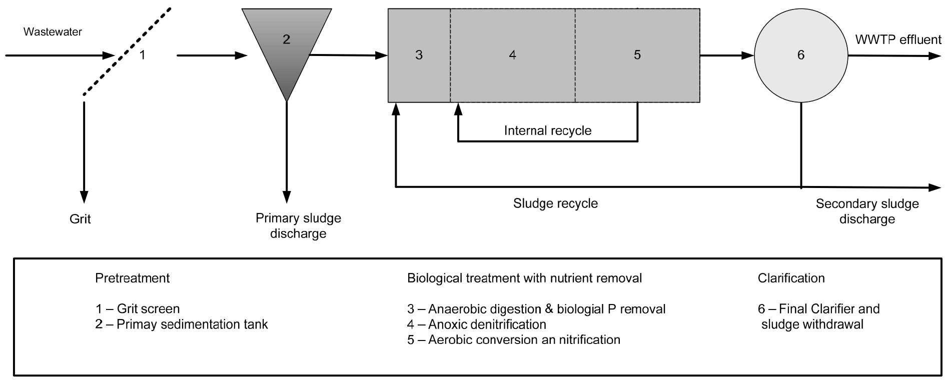

Figure 2.1 – Schematic flow scheme of an activated sludge process

2.2.2 Characteristics of WWTP effluent

The wastewater transported by the sewerage system and treated in a wastewater treatment plant consists of a mixture of municipal and industrial (pretreated) wastewater. Additionally, during storm weather events, the sewer is used for the transport of rainwater and is collected at the wastewater treatment plant. Considering these factors and the consequent variations in loads and concentrations of pollutants on different time and spatial scale an average influent quality for all wastewater treatment plants in the Netherlands is presented in Table 2.1.

Table 2.1 – Average quality of WWTP effluent in the Netherlands in 2007 and the current discharge standards

Parameter	Unit	Average concentration[1]	Discharge standards[2]
Chemical oxygen demand (COD)	mg O_2/L	43	125
Biochemical oxygen demand (BOD)	mg O_2/L	4	20 (without nitrification
Total nitrogen (N_{tot})	mg N/L	91	10 (> 20,000 pe) 15 (2,000 – 20,000 pe)
Total phosphorus (P_{tot})	mg P/L	1	1 (> 100,000 pe) 2 (2,000 – 100,000 pe)
Suspended solids (SS)	mg/L	11	30

1) Data 2007 (CBS, 2008)

2) VROM (1996)

Next to the constituents presented in Table 2.1 WWTP effluent contains a wide variety of trace compounds and elements, although they are not measured routinely. In Table 2.2 individual constituents are grouped into four broad categories: (1) the residual organic and inorganic colloidal and suspended solids, (2) dissolved organic constituents, (3) dissolved inorganic constituents and (4) biological constituents.

Table 2.2 – Typical residual constituents found in treated wastewater effluent and their impacts (Metcalf & Eddy, 2003)

Residual constituent	Effect
Inorganic and organic colloidal and suspended solids	
Suspended solids	- May cause sludge deposits or interfere with receiving water clarity - Can impact disinfection by shielding organisms
Colloidal solids	- May affect effluent turbidity
Organic matter (particulate)	- May shield bacteria during disinfection, may deplete oxygen resources
Dissolved organic matter	
Total organic carbon	- May deplete oxygen resources
Refractory organic	- Toxic to humans; carcinogenic
Volatile organic compounds	- Toxic to humans; carcinogenic; form photochemical oxidants
Pharmaceutical compounds	- Impact aquatic species (e.g., endocrine disruption, sex reversal)
Surfactants	- Cause foaming and may interfere with coagulation
Dissolved inorganic matter	
Ammonia	- Increases chlorine demand - Can be converted to nitrates and, in the process, can deplete oxygen resources - With phosphorus, can lead to the development of undesirable aquatic growths - Toxic to fish
Nitrate	- Stimulates algal and aquatic growth
Phosphorus	- Stimulates algal and aquatic growth - Interferes with coagulation - Interferes with lime-soda softening
Calcium and magnesium	- Increase hardness and total dissolved solids
Total dissolved solids	- Interfere with agricultural and industrial processes
Biological	
Bacteria	- May cause disease
Protozoan cyst and oocyst	- May cause disease
Viruses	- May cause disease

2.2.3 Particles in WWTP effluent

Particles in WWTP effluent are defined based on their size as dissolved, colloidal and suspended matter but there is not a sharp boundary in size that separates them. An overview of the different fractions, constituents and sizes of WWTP effluent is presented in Figure 2.2.

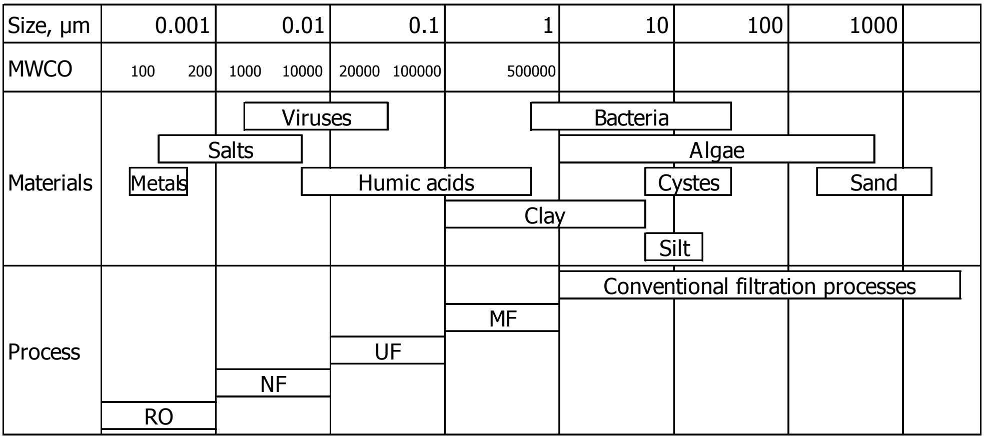

Figure 2.2 – Size of typical components in water and classification of membrane processes (adapted from van Dijk *et al.* 2001)

As written, there is not a sharp boundary between the particle sizes. Consequently there is some overlap between the same fractions. Van Nieuwenhuijzen (2002) classified wastewater constituents into different fractions: dissolved (< 0.1 µm), colloidal (0.45 µm – 2 µm), suspended (5 µm – 63 µm) and settable (> 63 µm). The fraction between colloidal and suspended was called supra colloidal and defined in the range 1.2 µm – 5 µm. However, other authors present different size ranges for the colloidal fraction. For example, Azema *et al.* (2002) and Levine *et al.* (1991) defined the colloidal fraction in the range of 0.001 µm – 1 µm and Metcalf and Eddy (2003) considered the colloidal fraction between 0.01 µm – 1 µm. Despite these different defined size ranges Adin (1999) reported that particles in WWTP effluent are mostly colloidal and negatively charged. This observation is confirmed by other researchers as well. For example, Abdessemed *et al.* (2002) showed that in WWTP effluent 58% of the organic load (COD) was found in a range larger than 0.1 µm, 13% of the COD was found within a range between 10 kDa and 0.1 µm and 29% was found in a fraction smaller than 10 kDa.

Also in this thesis to characterize WWTP effluent different fractions are distinguished. The classification of fractions is in line with earlier studies (Roorda, 2004; te Poele, 2005) and presented in Table 2.3.

Table 2.3 – Fractions distinguished in this thesis

Size (µm)	Fraction
> 0.45	Particles (suspended and settable material)
0.45 – 0.20	Colloids
0.20 – 0.10	Colloids
< 0.10	Dissolved material (macro molecules)

2.3 Membrane fouling

2.3.1 Definitions

As explained in chapter 1 membrane fouling is a natural consequence of the membrane separation process. The definitions of membrane fouling are several in literature and can be generally distinguished in two approaches. Some authors (van der Berg and Smolders, 1990 and Lojkine, 1992) use the term fouling to indicate strictly the 'tenacious' interactions that take place on the membrane and that would not be reversed by a release of the driving force (Ravazinni, 2008). The other approach includes within the term fouling each mechanism that leads to a decrease of performance during the filtration process. The approach, used in this thesis, is defined by the International Union for Pure and Applied Chemistry which defines fouling as *the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores* (Koros *et al.*, 1996). Within this definition fouling is encountered in the two terms: filterability and reversibility. Filterability as the loss of performance e.g. during a filtration run and reversibility as the extent to which membrane performance can be regained after it was fouled during filtration.

2.3.2 Fouling mechanisms

In the membrane filtration process of WWTP effluent different fouling mechanisms may occur. Generally, five fouling mechanisms can be distinguished; each mechanism contributes to the total resistance over the membrane. The fouling mechanisms are schematically presented in Figure 2.3:

- *Concentration polarisation (R_{cp})*: The increased concentration of rejected solutes near the membrane surface resulting in e.g. scaling, raise of osmotic pressure and gel formation.
- *Pore blocking (R_{pb})*: Particles enter the membrane pores and get stuck in their openings, so that the number of pore channels available for permeation is reduced.
- *Pore narrowing, e.g. by adsorption (R_a)*: Particles, colloids and macro molecules that enter the membrane pores and adsorb to the pore wall, resulting in less open pore channels and decrease of the permeate flow.
- *Cake layer formation (R_c)*: Particles, colloids and macro molecules accumulate on the membrane surface forming a more or less dense and more or less permeable layer. The strength of the cake layer depends on the interaction between the substances themselves and interaction with the membrane.
- *Compression of cake layer (R_{cc})* (not shown in Figure 2.3): If the cake layer is compressible an increase of trans membrane pressure will compress the cake layer resulting in a higher resistance.

The type of fouling is highly dependent on the type of filtration process, i.e. microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Concentration polarisation e.g. is of minor importance during dead-end ultrafiltration. The term originated from reverse osmosis applications and therefore left out of consideration in this thesis. Another fouling mechanism that is not incorporated in Figure 2.3 is the growth of micro organisms and their metabolic products of the membrane surface, so called biofouling. Once developed biofouling is very hard to remove as incomplete removal of (dead) micro organisms will spawn re-establishment of new biological activity (Schrader, 2006). Also in Figure 2.3 possible fouling mechanisms as compaction of membrane and capillary blocking are not included. Capillary blocking as fouling mechanism was established by Heijman *et al.* (2007). Heijman *et al.* (2007) investigated in a lab scale test whether there is heterogeneous fouling (capillary blocking) in dead-end ultrafiltration, the hydraulic cleaning with backflush and/or forward flush is not capable to remove all the cake fouling or pore blocking in the membrane module.

According to Figure 2.3 the total resistance (R_{total}) in equation 2.1 is based on the different fouling mechanisms and the initial membrane resistance, presented by a resistance-in-series relationship according to Bowen and Jenner (1995):

$$R_{total} = R_{membrane} + R_{cake} + R_{poreblocking} + R_{adsorption} \tag{2.1}$$

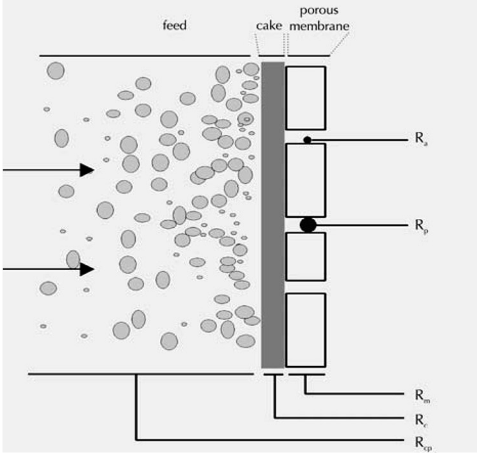

Figure 2.3 – The resistance of a fouled membrane by various fouling mechanisms, the driving force is from the left to the right: Ra = adsorption, Rp = pore blocking, Rm = initial membrane resistance, Rc = cake filtration, Rcp = concentration polarization (van den Berg, 1988)

2.3.3 Dynamics of the filter cake

In dead-end ultrafiltration of WWTP effluent cake filtration is assumed to be the predominant filtration mechanism for the increase of resistance (Roorda, 2004). Based on this assumption the total filtration resistance (R_{tot}) is the sum of membrane resistance (R_m) and cake resistance (R_c). Combining this assumption with the adapted Darcy's law (equation 1.2) the following relationship for the cake resistance can be derived (equation 2.2).

$$R_c = \frac{\Delta P}{\eta_t \cdot J} - R_m \tag{2.2}$$

in which:
R_c = cake resistance (m^{-1})
ΔP = trans membrane pressure (Pa) or (bar)
η_t = feedwater dynamic viscosity (Pa·s)
J = flux ($m^3/m^2 \cdot s$)
R_m = membrane resistance (m^{-1})

The membrane resistance is considered as constant but the cake resistance increases due to the retention of particles within the cake layer. This is shown in equation 2.3. It assumes that material rejected by the membrane forms a cake layer, which causes cake resistance to increase proportionally to the amount of material delivered to the membrane surface.

$$R_c = \alpha_{av} \cdot c_v \cdot \frac{V}{A_m} \tag{2.3}$$

in which:
α_{av} = average specific cake resistance (m/kg)
c_v = solids concentration in feedwater (kg/m^3)
V = permeate volume (m^3)
A_m = membrane area (m^2)

The compressibility of the formed cake layer during dead-end ultrafiltration of WWTP effluent was investigated by Roorda (2004) and Zheng, *et al.* (2010). Both authors indicate that the cake layer is compressible using equation 2.4. Therefore an increase of trans membrane pressure will result in more compression leading to a higher specific fouling resistance and a lower reversibility (Zheng, *et al.*, 2010).

$$\alpha_{av} = \alpha_0 \cdot \Delta P^s \tag{2.4}$$

in which: α_0 = specific cake resistance at reference pressure (m/kg)

s = compressibility coefficient (s = 0 refers to no compression, the increase of s represents the layer is more compressed, s = 1 refers to complete compression)

2.4 Factors affecting fouling

As already mentioned the fouling mechanisms will result in a performance decrease of the separation step. The operational performance of membrane filtration is a function of time and many other variables. In general there are three major variables influencing membrane fouling: feedwater properties, operational conditions and membrane characteristics (Amy, 2008). Table 2.4 summarizes the main factors involved in the fouling process for each of these three variables.

Table 2.4 – Factors influencing membrane fouling

Feedwater properties	Operational conditions	Membrane characteristics
Chemical and physical properties feedwater solution	Flux	Clean water flux and/or resistance
Chemical properties of particles, colloids and dissolved material	Recovery	Pore size or molecular weight cut off
Particle size distribution	Pretreatment	Hydrophobicity/hydrophilicity
	Chemical cleaning	Surface charge
	Hydraulic flushes	Surface morphology

2.4.1 Feedwater properties

The potential membrane foulants in WWTP effluent can be present in the influent of the wastewater treatment plant, or originate from the activated sludge (particulate material) and bacterial metabolism. During the biological treatment the particle size distribution in wastewater changes as a result of new cell synthesis, flocculation, adsorption, enzymatic breakdown of macro molecules and biochemical oxidation (Levine *et al.*, 1985). Usually and also presented in Figure 2.1 the biomass and the biologically treated water (WWTP effluent) are separated by gravity in the final clarifier. Generally, the WWTP effluent consist of mainly organic compounds, suspended solids and nutrients (Metcalf and Eddy, 2003). In Table 2.5 an overview of these components is presented adopted from te Poele (2005) and Metcalf and Eddy (2003).

Table 2.5 – Constituents found in WWTP effluent that influence membrane fouling

Soluble biodegradable organics	- Organics that escaped biological treatment. - Organics formed an intermediate products in the biological degradation of the waster. - Cellular components as a result of cell death or lysis .
Suspended organic material	- Biomass produced during treatment that escaped separation in the final settling tank. - Colloidal organic solids in the wastewater plant influent that escaped treatment and separation.
Nitrogen and phosphorus	- Contained in biomass in effluent suspended solids. - Soluble nitrogen as NH_4-N, NO_3-N, NO_2-N and organic–N. - Soluble orthophosphates.
Non biodegradable organics	- Those originally present in the wastewater influent. - By-products of biological degradation

2.4.1.1 Organic fouling

From the constituents presented in Table 2.5 the organic compounds are mostly associated with fouling of ultrafiltration membranes. Fouling caused by these constituents (organic fouling) can be distinguished in three types (Amy, 2008) for drinking water treatment and wastewater reclamation/reuse:

- *allochthonous natural organic matter* (NOM) dominated by humic substances derived from runoff and leaching of vegetative debris from terrestrial sources within a watershed;
- *autochthonous or algal organic matter* (AOM) consisting of extracellular and intracellulare macromolecules and cellular debris;
- *wastewater effluent* (EfOM) consisting of background (drinking water) NOM plus soluble microbial products (SMPs) derived from biological wastewater treatment.

During filtration of WWTP effluent EfOM deposits on or in the membranes, reducing the permeate rate by the different filtration mechanisms. In particular the soluble microbial products (SMP) and/or (soluble) extracellular polymeric substances (EPS) are considered as the major foulants of EfOM during ultrafiltration of WWTP effluent (Jarusutthirak and Amy, 2001; te Poele, 2005; Rosenberger, *et al.*, 2005; Jarusutthirak and Amy, 2007; Haberkamp, *et al.*, 2008; Zheng *et al.*, 2010). Both, SMP and (soluble) EPS are considered as similair substances. Laspidou and Rittmann (2002) compared the concepts of soluble EPS and soluble SMP and concluded that both are indeed identical. Furthermore, because of the analytical methods for their determination, soluble SMP and soluble EPS cannot be distinguished in engineering practice (te Poele, 2005). Both substances are produced by micro organisms and released into the liquid phase as part of the metabolism and due to biological or mechanical stress (te Poele, 2005). However, with respect to EPS two basic forms are distinguished: bound (or extracted EPS) or soluble EPS (Geilvoet 2010). Bound extracellular polymeric substances are of a biological origin, participate in the formation of microbial aggregates and consist of insoluble materials (sheats, capsular polymers, condensed gel, loosely bound polymers and attached organic material) (Laspidou and Rittmann 2002). Soluble EPS and

SMP consists of soluble macro molecules, colloids and slimes (te Poele, 2005) and can be defined as “the pool of organic compounds that are released into the solution from substrate metabolism (usually with biomass growth) and biomass decay” (Barker and Stuckey, 1999). The main components of soluble EPS and SMP are proteins and polysaccharides and to a minor extent, nucleic acids and lipids (Flemming and Wingender, 2001).

Which compound of SMP, either proteins or polysaccharides, are most strongly linked to membrane fouling is still an open question. For example, te Poele (2005) has demonstrated that the smaller colloids or organic molecules (< 0.10 µm) of WWTP effluent predominantly influence the reversibility during ultrafiltration. These organic molecules had a protein origin and the influence of polysaccharides was not clearly demonstrated. This observation was also noticed by Haberkamp (2008). In that research a model solution mixed with a natural EPS extract and real WWTP effluent were filtrated during cross flow filtration experiments. The model solution with bacterial EPS extract contained significantly more polysaccharides than proteins, whereas the WWTP effluent contained a larger proportion of proteins. The ultrafiltration of WWTP effluent resulted in a higher flux decline than the EPS model solutions. Therefore, it was indicated that proteins play an important role in ultrafiltration membrane fouling.

Other researchers underline the negative impact of proteins but take the effect of polyasaccharides and proteins in one term as biopolymers together. Zhing *et al.* (2009a) found during stirred cell experiments that dissolved substances of WWTP effluent larger than the ultrafiltration pore size attribute to more than 50% of the total fouling resistance. Within the dissolved substances, the concentration biopolymers detected by LC-OCD shows a quantitative correlation with the filterability of water samples in dead-end ultrafiltration. During the filtration process, biopolymers cover membrane pores firstly and lead to a steep flux decline. The impact of polysaccharides and colloids was shown by Jarusutthirak and Amy (2006) during the characterisation of different EfOM fractions in fouling of ultrafiltration and nanofiltration membranes. In addition, Cho *et al.* (1998) characterised clean and NOM fouled ultrafiltration and nanofiltration membranes and indicated polysaccharides or polysaccharide like substances as foulants.

Although the main components of soluble microbial products are the proteins (60%) and polysaccharides (40 – 95%) (Flemming and Wingender, 2001) also humic substances are a major part (Drewes and Fox, 1999; Hezjlar and Chudoba, 1986). Humic substances or fulvic substances are composed of phenol compounds, single sugars and amino acids and bound with ether, carbon and peptide bonds. Compared to the proteins and polysaccharides, humic substances are considered of minor relevance during ultrafiltration of WWTP effluent (Laabs *et al.*, 2006; Haberkamp *et al.*, 2008).

2.4.1.2 Size of organics

As stated in the previous section various researchers report that fouling is predominantly determined by soluble microbial products in WWTP effluent. To analyse SMP in WWTP effluent different methods (specific UV-absorbance, total organic carbon, colorimetric analyses and size exclusion chromatography) are applied but all these methods solely provide information about the characteristic concentration and not about the characteristic size. Therefore also investigations to characterize the size of (organic) colloidal particles causing fouling during ultrafiltration of WWTP effluent are performed by several researchers. Roorda (2004) performed SUR tests with different fractions of WWTP effluent and showed that the fraction between 0.1 – 0.2 µm predominantly determined the filtration characteristics. This finding is confirmed by research of te Poele (2005). Te Poele (2005) stated that organic colloids of size fraction < 0.45 and 0.10 µm reveal to be of major influence on the filterability. It is assumed that these colloids might possibly be cell fragments and large molecules (te Poele, 2005), which could not be measured by analytical methods like specific UV-absorbance, total organic carbon, colorimetric analyses and size exclusion chromatography. Furthermore, te Poele (2005) stated that the reversibility is mostly influenced by organic molecules (mainly proteins) < 0.10 µm. These findings of Roorda (2004) and te Poele (2005) underline the need to focus on both aspects of organic fouling: concentration and size. Therefore in this thesis the colorimetric analyses will be accompanied by fractionation tests in order to obtain a better understanding of fouling formation during ultrafiltration of WWTP effluent.

2.4.1.3 Divalent cations, pH and ionic strength

In addition to the composition and concentration of EfOM substances the concentration of divalent cations, pH and ionic strength influence the impact of organic fouling. The pH and ionic strength composition of feedwater influence the chemical interactions between the foulants and the membrane and between the foulant and fouling layer (Costa *et al.*, 2006) Divalent cations like calcium and magnesium bridges with negatively charged functional groups within the bacterial EPS, which helps to aggregate and stabilize the matrix of biopolymer and microbes (Kim and Jang, 2006). This mechanism may result in a network structure of EPS on the membrane surface influencing the filtration rate.

2.4.2 Operational conditions

2.4.2.1 Operating mode

The permeate flux can be regarded as a measure for the fouling load on the membrane, because it determines how much foulants are transported towards the membrane. This unavoidable transport during permeation can be generally performed in three different operation modes: with constant trans membrane pressure, with constant permeate flux or with a combination of these. During constant trans membrane pressure operation the flux will decrease over time and during constant flux operation the trans membrane pressure will increase over time. In the case of no fouling there will be no difference between both operation modes but from an engineering practice point of view the use of constant flux is preferable instead of constant trans membrane pressure. However many researchers use constant pressure operation for the benefit of conducting simple short term experiments (Lee *et al*., 2008). Whether the constant flux or the constant trans membrane pressure is more beneficial for fouling control is a difficult question. On the one hand different authors (Loijkine *et al*., 1992; Bourgeos *et al*., 2001; Tarabara *et al*., 2002) prefer for different reasons constant pressure but on the other hand other authors (Defrance and Jaffrin, 1999; Ho and Zydney, 2002) suggest constant flux as it usually results in higher permeate volume production. Differently, Vyas *et al*. (2002) suggest a combination of constant flow and constant pressure, which seems favourable to minimise fouling and optimise process performance.

2.4.2.2 Hydraulic flushes

As a result of the dead-end mode the membrane has to be cleaned often in order to remove the rejected compounds. The period (filtration run) between two hydraulic flushes may vary between 10 and 60 minutes depending on the feedwater quality, but a filtration period of 30 minutes is usually applied in practice. Depending on the type of hydraulic flush either feed water, permeate or ultrapure water are flushed into the membranes. The different types of hydraulic flushes are a forward flush (FF) and back flush (BF) as illustrated in Figure 2.4.

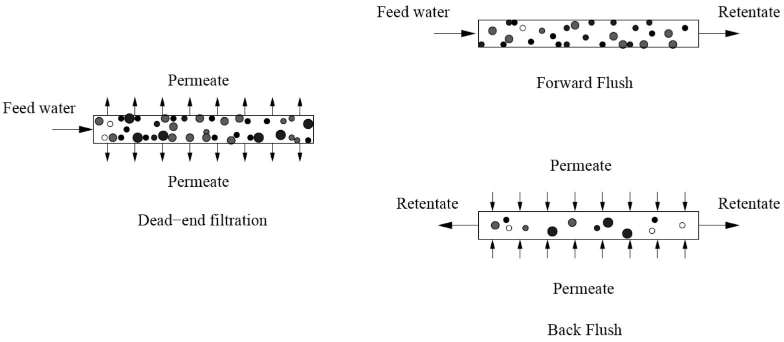

Figure 2.4 - Schematic drawing of hydraulic cleaning: forward flush and back flush (te Poele, 2005)

The forward flush is a turbulent cross flow along the feed side of the membrane surface. With small diameters of membrane fibres high cross flow velocities are needed to obtain turbulent flow. This velocity is many times higher compared to the velocity during dead-end filtration. A mixture of air and water can be used to improve the forward flush. The air is used to create turbulent flow in the membrane under process conditions where no turbulence is attained with the water flow. The air/water flush is patented as the AirFlush® and further investigated by Verberk (2005). For a forward flush feed water can be used in order to obtain a high recovery.

The back flush or backwash is a permeate flow reversed to the filtration mode. As a result, the retained material in the membrane pores and on the membrane is released. Permeate is used for the back flush in order to keep the permeate side of the membrane free of particles. The back flush flux is normally 2 to 2.5 times the flux during filtration. Typical duration of the back flush is 30 to 60 seconds. After removing the retained material from the pores and membrane surface it has to be transported out of the module. Because the amount of permeate used for back flush is limited (because of recovery) the transport of retained material may be insufficient. A combined back flush and forward flush can be used to overcome this problem.

2.4.2.3 Chemical cleaning

In order to maintain an optimal flux, membranes are often cleaned by periodical hydraulic flushes. Nevertheless after several filtration periods the performance declines, in spite of frequently applied hydraulic flushes. In that case the membranes need to be cleaned chemically in order to recover the flux to initial or acceptable values. The concentration of the chemicals and the cleaning time are important parameters for efficient use of a chemical cleaning procedure. In order to prevent membrane degradation during a chemical cleaning, the chemical properties of the membrane should be known. Effective cleaning must inhibit the redeposition of the foulants on the membrane surface. The chemicals that are used for cleaning can be classified in the following way (Table 2.6).

Table 2.6 – Classification of chemical cleaning agents and their mechanisms (te Poele, 2005)

Cleaning agent	Mechanism
Acid	Removing of crystallised salts, metal oxides and metal hydroxides.
Alkali	Removing of general organic fouling.
Active chlorine	Active chlorine as the active component to minimise organic fouling and micro-organisms.
Oxide	Oxide as the active component to diminish mainly organic fouling and micro-organisms, but can also be used to minimise other types of fouling.
Organic solvent	Removal of organics by solubility
Enzyme	Specific enzyme degrades specific organic foulants.

Beside the periodical chemical cleaning (often called chemical enhanced back flush) which is part of the automated process control of the installation also a more intensive cleaning might be necessary. The so-called “cleaning in place” (CIP) can last from a few hours to several days and is most of the time not automated. If the CIP is not able to clean the membranes, the membranes are replaced by new ones.

2.4.3 Pretreatment

The integration of an extra treatment step (pretreatment) in front of the membrane process is an important trend in the development of membrane filtration to improve the performance. In this thesis pretreatment refers to the operation of processes that are conducted in precedence to membrane filtration to improve the performance of membranes during filtration of WWTP effluent. Beside the improvement of the performance pretreatment is sometimes applied to enhance the rejection efficiencies. However, predominantly pretreatment is applied to control membrane fouling (Huang *et al.*, 2007).

In a paper of Huang *et al.* (2007) the mechanisms of pretreatment are summarized by three types of effect:

- *Physical effects*: pretreatment can increase the size of aquatic substances by aggregation (i.e., coagulation) or adsorbing them onto materials larger than membrane pore dimensions thereby enhancing their rejections by membrane filtration and reducing membrane fouling.
- *Chemical effects*: pretreatment can alter the nature (i.e., prefiltration, coagulation or adsorption) and magnitude (coagulation and softening) of interfacial interactions involved in the subsequent membrane filtration and mitigate the impact of undesirable interactions between aquatic substances and membrane surfaces.
- *Biological effects*: pretreatment can either enhance positive impacts (i.e., reduction of organic contaminant concentration in the feedwater by biodegradation) or reduce negative impacts (i.e., disinfection of feedwater to reduce biofilm formation) of biological processes in the performance of membrane filtration.

The effects are not strictly separated in process operations of pretreatment. Some pretreatment processes can have multiple effects on membrane filtration. For example, coagulation may results in two effects. Firstly, an increase of the particle size by the aggregation of aquatic substances (physical) and secondly a chemical reduction of dissolved and colloidal organic matter that may attribute to irreversible fouling (te Poele, 2005).

In general coagulation, prefiltration and adsorption are the most widely used pretreatment technologies in full scale applications. Beside these technologies oxidation and ion exchange are getting more attention. In the following sections the different pretreatment technologies are presented.

2.4.3.1 Coagulation

Metcalf and Eddy (2003) define coagulation as the process of destabilizing colloids and particles so that particle growth can occur as a result of particle collisions. Strictly the word coagulation refers to the destabilization process and the word flocculation to the formation of aggregates (flocks) consisting of destabilized colloidal and particulate matter and precipitated hydroxides. In this thesis coagulation is used as a general term that includes both destabilization and flocculation. Most commonly cationic or metallic coagulants like aluminium and ferric salts are used for pretreatment. The operation of coagulation for membrane filtration can be directly (or so called direct in-line coagulation) or in combination with sedimentation or filtration. During these separation steps particles subject to membrane filtration can be effectively removed. Therefore the feedwaters after coagulation-sedimentation/filtration usually cause less fouling than raw feedwater (Huang *et al.*, 2007). Roorda (2004) investigated the performance of an ultrafiltration pilot installation in combination with coagulation-filtration as pretreatment. Although some increase of performance was obtained, Roorda (2004) concludes that the technologies did not efficiently remove the 0.1 – 0.2 µm particles, which is the fraction that predominantly determines filtration characteristics. Direct in-line coagulation with ferric chloride was investigated by Decarolis *et al.* (2001) on pilot scale with a dead-end ultrafiltration system. This research showed that ferric chloride pretreatment enhanced membrane productivity by increasing particle floc size, which led to decreased pore plugging, reduced cake layer resistance and enhanced backwashing efficiency.

2.4.3.2 Prefiltration

In this thesis prefiltration as pretreatment for ultrafiltration and microfiltration involves the use of conventional packed bed filters i.e. rapid sand filters, dual media filter etc. Its main purpose is the removal of suspended (including coagulated flocs) and colloidal matter from raw WWTP effluent. Many authors (de Koning and van Nieuwenhuijzen, 1999; Bourgeous *et al.*, 2001; Roorda, 2004; te Poele, 2005; Fan, *et al.*, 2008) have reported about the effectiveness of prefiltration prior to ultrafiltration or microfiltration. De Koning and van Nieuwenhuijzen (1999) investigated the performance of the combination flocculation – filtration – ultrafiltration at two WWTPs (WWTP Ede and WWTP Elburg) in the Netherlands. Although the prefilter did not produce high removal efficiencies it appeared to be an important part of the total polishing concept. However, the results differed at the two treatment locations. At the WWTP Elburg prefiltration was required to achieve constant high fluxes and reliable operation at constant trans membrane pressure. Without prefiltration the flux rapidly decreased from an average of 90 $L/m^2 \cdot h$ to a low level of 40 $L/m^2 \cdot h$, without successful hydraulic cleaning procedures. Only chemical cleaning was effective for a short term. At the WWTP Ede successful and stable operation of ultrafiltration was possible at a trans membrane pressure of 0.6 – 0.9 bar without prefiltration. Nevertheless the content of suspended solids was higher in the effluent of WWTP Ede compared to WWTP Elburg. Therefore the authors suggested that the filterability of WWTP effluent is not related to amount of particles or suspended solids but effected by local circumstances. This phenomenon has been further investigated by Roorda (2004) who concluded that multi media filtration slightly improves the filterability of WWTP effluent with a maximum of 25%. But multi media filtration did not effectively decrease the 0.1 – 0.2 µm fraction of WWTP effluent. This fraction is not measured during the analyses of turbidity and suspended solids. The results of Roorda (2004) have been confirmed by research of Bourgeous *et al.* (2001) and te Poele (2005). Bourgeous *et al.* (2001) showed that a thin cake layer developed for ultrafiltration of effluent after prefiltration, while a thicker cake layer developed for raw WWTP effluent. The thinner cake layer showed better filterability and was completely removed by a regular back flush. The cake layer found for raw WWTP effluent could not be removed completely with a backflush because of clogging membrane fibers. More or less the same observation was obtained by Fan, *et al.* 2008. Lab scale experiments showed that the combination of coagulation and prefiltration (1.5 µm) resulted in better ultrafiltration and microfiltration performance compared to coagulation-sedimentation and direct in-line coagulation.

Next to the mentioned prefiltration techniques, recent work has shown biofiltration as a promising pretreatment technology to reduce fouling (Mosqueda-Jimenez, 2006 and Huck and Sozański, 2008). Treatment combinations of natural biofiltration i.e. bank filtration and soil aquifer treatment and ultrafiltration/microfiltration are rarely applied in advanced water treatment. Nevertheless biofiltration processes offer simple and cost effective measures to reduce the content of bio available organic compounds (Zheng *et al.*, 2009b). This effect has been shown by Zheng, *et al.* (2009b) with respect to the removal of biopolymers of WWTP effluent. Slow sand filtration of WWTP effluent removed the biopolymer peak and therefore decreased the fouling potential of water samples to ultrafiltration membranes.

2.4.3.3 Adsorption

In the context of this thesis adsorption refers to the use of activated carbons and other “pre-formed” adsorbents in precedence to membrane filtration. The adsorption process itself involves the uptake of aquatic substances by the surface of the activated carbon. Due to the high porosity and dispersity activated carbon has a relatively large specific surface area. In combination with ultrafiltration and microfiltration activated carbon can have two functions. Firstly, adsorption of small substances of WWTP effluent that can poorly be removed by the membranes. These substances can be of different origin e.g. humic substances, micropollutants, (organically bounded) heavy metals, etc. Secondly, the adsorbents may also serve as competitor with organic matter that can cause membrane fouling once being adsorbed on membrane surfaces (Crozes, *et al.*, 1993).

Generally, activated carbon for water treatment can be separated in two size classifications: powdered activated carbon (PAC), which typically has a diameter of less than 0.074 mm, and granulated activated carbon, which has a diameter of larger than 0.1 mm (Metcalf and Eddy, 2003). The most intensively studied size for membrane filtration is probably powdered activated carbon. PAC is added into the feedwater to adsorb the small substances; it can be effectively rejected by ultrafiltration/microfiltration as its size is significantly greater than the membrane pores. Consequently, PAC in the membrane concentrate may be recycled to maintain enough adsorbent concentration in feedwater. GAC is mostly applied in precedence to ultrafiltration/microfiltration in a filterbed and operated like a discontinuous sand/anthracite filter. This process is also referred to the name adsorptive filtration (Roorda, *et al.*, 2005).

In respect to PAC and the effect on membrane fouling different findings are reported in the literature. In general it seems that the effect depends on the membrane material, operation mode, membrane configuration and type of feedwater. Mozia *et al.* (2005) tested the influence of PAC addition on flux decline of three different polymer ultrafiltration membranes. The tested membranes were prepared from polysulfone (PSF), cellulose acetate (CA) or polyacrylonitrile (PAN). The researchers presented the combination of PAC addition and membranes formed of PAN as most favourable considering the effectiveness of organics removal and the permeate flux. In contrast an earlier study performed by Lin *et al.* (1999) showed a significant decrease of flux of negatively charged polysulfone membranes due to PAC addition. One of the main differences between both studies was the applied membrane configuration; Lin *et al.* (1999) used a hollow fibre while Mozia *et al.* (2005) tested a flat sheet membrane. The optimization of the PAC-UF configuration in terms of increase of backwash pressure, greater linear velocity, feedwater direction and proper module design was also suggested by Oh *et al.* (2006) to get a suitable integrated system. Nevertheless good experience regarding ultrafiltration fouling control of WWTP effluent and PAC addition was obtained by Shon *et al.* (2004a) and Haberkamp *et al.* (2007). Shon *et al.* (2004a) presented similar reduction of flux decline for both flocculation and PAC adsorption. In spite of the same effect the underlying mechanisms were different. Flocculation resulted in higher reduction of colloidal matter and larger molecules than with PAC adsorption. The flocculation also achieved a removal of a portion of small molecular weight organics through the mechanisms of adsorption and complexation (Shon *et al.*, 2004a). The PAC adsorption played a major role in removing small organics only. The removal of the colloidal portion (between 3500 Da to 0.45 μm) by adsorption was not significant. Haberkamp *et al.* (2007) observed as well a positive affect of PAC addition on flux decline during ultrafiltration but remarked that increased demand of activated carbon due to considerable consumption of adsorption capacity by low molecular weight substances, which do not presumably contribute tot membrane fouling, may be a limiting factor for the application of adsorption as the pretreatment process for fouling reduction.

Compared to the application of PAC addition less research is published about the use of granulated activated carbon (GAC) filtration in precedence to ultrafiltration and microfiltration. Nevertheless GAC and biological activated carbon filtration (BACF) give important perspectives in minimizing organic fouling. The main distinction between BACF and GAC filtration is the removal mechanism. BACF combines adsorption and biodegradation where GAC filtration only implies adsorption as a removal mechanism.

Regarding GAC filtration, Tsujimoto *et al.* (1998) found that this pretreatment step reduced irreversible fouling of ultrafiltration membranes treating a natural surface water. The combination of GAC – (cross flow) ultrafiltration and biologically treated sewage effluent was investigated by Shon *et al.* (2004b). In this study this combination was compared with other pretreatment steps for ultrafiltration: flocculation, PAC adsorption and flocculation followed by PAC adsorption. Compared to the other pretreatment technologies the flux decline after GAC filtration was more but it was still significantly better than raw biologically treated sewage effluent. The combination of GAC filtration and airflushed microfiltration with WWTP effluent was also subject of research by Roorda *et al.* (2005). In terms of stable operation performance the researchers found adsorptive filtration one of the best pretreatment steps for microfiltration.

2.4.3.4 Alternative pretreatment technologies

Advanced Oxidation Processes

In water treatment applications, advanced oxidation processes usually refer to a specific subset of processes that involve ozone (O_3), peroxide (H_2O_2), and/or ultra violet (UV) light. Usually only ozonation is applied for the treatment of wastewater. Park (2002) investigated ozonation of chemical wastewater as pretreatment for UF. It was concluded that the flux rate increased as the amount of ozone increased. Seo *et al.* (2001) concludes for ceramic membranes ozone is effective to control the membrane fouling by the increased organic degradation.

Ion exchange

Application of magnetic ion exchange (MIEX®) resin to membrane filtration has been studied at different scales in the past few years. Zhang *et al.* (2006) tested MIEX® as pretreatment to a submerged membrane system in the treatment of biologically treated wastewater. It was found that MIEX® resin could effectively remove the small molecular weight (500 – 1000 Da) organic matter and the hydrophilic portion of DOC. At optimal concentration MIEX® could remove as much as 60% of DOC in the wastewater resulting in a longer operational time of the membrane process. Combining MIEX® and PAC adsorption could even increase the removal rate (TOC removal of 80%). Generally the effect of MIEX® on ultrafiltration and microfiltration seems to be positive though the major mechanisms are unsolved.

Precoat

Removal of the 0.1 to 0.2 μm fraction might be done by the formation of a precoat (e.g. Diatomite, Powdered Activated Carbon (PAC), Kaolinite or iron oxide) on the membrane that acts as secondary membrane. Enhanced Pre-Coat Engineering (EPCE) results in a better restoration of the permeability after a backwash. Bigger particles seem to restore the membrane better after a backwash or enhanced backwash. Smaller particles seem to give a lower rate of fouling. EPCE is a promising technique to increase membrane performance (Galjaard *et al.*, 2001).

Integrated pretreatment technologies

As discussed previously, pretreatment technologies often remove only a certain type or range of compounds in WWTP effluent. It is, therefore, reasonable to consider that proper integration of multiple pretreatment can combine the benefits of each separate pre-treatment technology. For example, the technologies, coagulation – PAC adsorption – ultrafiltration are presented by different researchers (Shon *et al.*, 2004a and Haberkamp *et al.*, 2007) as an optimal combination in terms of flux decline and DOC removal. Roorda (2004) and te Poele (2005) presented coagulation – multi media filtration – ultrafiltration as a good integrated concept for stable operation performance. Generally, integration of pretreatment technologies can provide better feedwater quality for membranes, but the costs of the entire system may increase drastically (Huang *et al.*, 2007).

2.4.4 Membrane characteristics

The effective pore size (Lozier *et al.*, 2008) and surface charge of membranes (Schafer *et al.*, 1998) are considered to be significant factors contributing to the reduction of permeate flux The effective pore size of a membrane is a membrane characteristic affecting the decrease of permeate flux. The lower the molecular weigh cut off (MWCO), the larger the membrane resistance. A negatively charged membrane will electrostatically repulse negatively charged functional groups associated with EfOM (Jarusutthirak and Amy, 2001). The more negative charge density on the membrane surface is correlated to the greater hydrophilicity of the membrane. Therefore, a less negative surface charge (more hydrophobic) may increase the deposition of hydrophobic EfOM leading to more adsorptive fouling.

The interaction between EfOM and the membrane characteristics like surface charge and MWCO has been investigated by Jarusutthirak and Amy (2001). They established a dependency of the flux decline, EfOM rejection and fouling mechanisms on the charge of membrane surface and the MWCO. The negatively charged surface led to the adsorption of the hydrophobic portion of EfOM.

The effect of the pore size of membranes on the retention of foulants of WWTP effluent is presented by Laabs *et al.* (2006). During filtration experiments with ultrafiltration membranes (pore size of 10 nm) the substances (organic colloids, polysaccharides and proteins) eluting in the polysaccharide peak of a size exclusion chromatogram changed completely e.g. the feedwater exhibits a clearly polysaccharide peak, the permeate sample contains no substances in this molecular weight/size range. But during the same experiment with microfiltration membranes (pore size of 50 nm) the substances of the polysaccharide peak remained in the filtrate. Therefore Laabs *et al*. (2006) suggested that the fouling rate depends on the pore size of the membranes even when the size of the pores differs a little.

2.5 Fouling indicators and predictions

As written in chapter 1 the performance of the ultrafiltration process is determined by both filterability of the feedwater and by reversibility of the fouling layer. Both parameters are affected by the operational conditions and membrane characteristics but the more fundamental cause for membrane fouling are the properties of the feedwater. Therefore many researches (Boerlage *et al*., 2003; Roorda, 2004; Rosenberg *et al.,* 2005; Park *et al*., 2006; Kim and DiGiano, 2006 and Huang *et al*., 2008) underline the need for a general method to measure and predict the fouling potential of the feedwater to membrane filtration system. Such a method can be used at the design stage to assess required pretreatment and later to monitor the effectiveness and performance of a pretreatment system during plant operation (Park *et al*., 2006). Ultimately the fouling indices enable engineers to determine the design requirements without conducting pilot studies which need considerable time and expenses. There have been attempts to establish tests and indices to describe the filterability, respectively fouling potential of feed suspensions and solutions (Rosenberg *et al*., 2005):

- On-line measurements of flux and trans membrane pressure during continuous filtration can be used to calculate the fouling rate (slope of resistance over time). This can be done either in batch experiments (e.g. with side-stream modules) or in situ.
- Time to filter (TTF), modified fouling index (MFI), specific resistance to filtration (SRF) and specific ultrafiltration resistance (SUR) are used to describe filterability. Recently the unified modified fouling index (UMFI) is added to this list as a parameter to describe both filterability and reversibility. All these tests are based on the theory of cake filtration and are usually performed in dead-end mode on lab or bench scale.

2.5.1 Bench and lab scale tests

In this section briefly the MFI-(UF), UMFI and SUR are discussed.

2.5.1.1 Modified filtration index-(UF)

The MFI is measured in dead-end mode with a microfiltration membrane (0.45 μm) at constant pressure (2 bar) and continous measurement (every 30 seconds) of the produced filtrate. According to the cake filtration model (Hermia, 1982) at constant pressure the following relation between filtration time and filtrated volume can be derived (Mulder, 1996):

$$\frac{t}{V} = \frac{\eta \cdot R_m}{\Delta P \cdot A} + MFI \cdot V \tag{2.5}$$

in which: t = filtration time (s)

V = filtrate volume (m^3)

η = water viscosity (N s/m^2)
R_m = membrane resistance (m^{-1})
ΔP = applied trans membrane pressure (bar or N/m^2)
A = membrane surface area (m^2)
MFI = membrane fouling index (s/m^3)

Equation 2.5 predicts a linear relationship between t/V and V during cake filtration. A high value of MFI indicates rapid fouling of the membrane.

The MFI is further developed by Boerlage *et al.* (2003) to the MFI-UF to measure and predict the particulate fouling potential for different feedwaters in membrane filtration installations. A disadvantage of the MFI-UF is the applied pressure. This pressure is 2 bar which is about 4 times more than usual in ultrafiltration applications. Especially during tests with WWTP effluent the applied pressure will result in unrepresentative values due to the compression of the formed cake layer.

2.5.1.2 Unified Membrane Filtration Index

The Unified Membrane Filtration Index (UMFI) has been recently reported by Huang *et al.* (2008) and presented as a parameter to quantify and compare the fouling on different scales (e.g., lab, bench and full scale) and different units (e.g., stirred-cell versus hollow fiber bench scale units). A value of UMFI (m^2/L) can be estimated from a data plot of inversed normalized flux (J_s/J_{s0}) versus hydraulic throughput (L/m^2) as shown in equation 2.6. Like the other filtration indices the UMFI is based on solely cake filtration and Darcy's law.

$$\frac{1}{J_s{}^{'}} = 1 + \left(\frac{\alpha_c C_f}{R_m}\right) V_s \tag{2.6}$$

in which:
$J_s{}^{'}$ = normalized specific flux (-)
α_c = specific cake resistance (m^{-1})
C_f = concentration of foulants (kg/m^3)
R_m = membrane resistance (m^{-1})
V_s = permeate throughput (L/m^2)

Based on this relationship, UMFI (m^2/L) is defined as follows:

$$UMFI = \frac{\alpha_c C_f}{R_m} \tag{2.7}$$

For a filtration without hydraulic backwash, UMFI is related to the hydraulic property of the cake layer (α_c), the concentration of total foulants (C_f) and the hydraulic property of the clean membrane. Its value is not affected by the operating mode. Temperature effects are also canceled out through the normalization of specific fluxes. If the concept is applied to a filtration with either frequent hydraulic backwashes or chemical cleaning (as with the pilot systems), the UMFI can still be calculated as a measure of the rate of hydraulically irreversible fouling or chemically irreversible fouling that occurs within certain unit permeate throughputs.

A critical note concerning the UMFI is that the value depends on the hydraulic property of the clean membrane (R_m). As a consequence it means the UMFI is not universal but differs for each type of membrane.

2.5.1.3 Specific Ultrafiltration Resistance

To measure the filterability of WWTP effluent Roorda (2004) developed a parameter called Specific Ultrafiltration Resistance (SUR). The SUR is calculated from the slope of a filtration curve (t/V versus V) that is measured in a period of 30 minutes of filtration over an ultrafiltration membrane at a constant temperature (~ 20 °C) and a trans membrane pressure (TMP) of 0.5 bar. The parameter is used during the experiments presented in this thesis and therefore is described in detail in chapter 3.

2.5.1.4 Vito Fouling Measurement

The Belgian company VITO (Flemish Institute for Technological Research) developed a filtration characterisation method called the Vito Fouling Measurement (VFM) (Braun *et al.*, 2005). In contrast to the MFI-(UF), UMFI and SUR the VFM aims to characterise (by mathematical processing) all (complex) fouling phenomena (Brauns *et al.*, 2002) instead of only cake filtration. As a consequence the VFM measurement does not results in one value like the MFI-(UF), UMFI and SUR but it will give a graphical presentation. By comparing filtration graphs of different types of feedwater information is gained about the fouling potential. However, since cake filtration is considered as the predominant mechanism during ultrafiltration of WWTP effluent (Roorda, 2004) this approach will not provide much extra information compared to the MFI-(UF), UMFI and SUR.

2.5.2 On-line measurements

In full scale or pilot installations, the filterability is measured in a different way. The filterability is measured as fouling rate (dR/dt) which is the increase in filtration resistance over time after one filtration period (see Figure 2.5) The filterability can be derived from on-line measurements of flux, TMP and temperature (te Poele, 2005), see equations 2.8 and 2.9

$$\frac{dR}{dt} \tag{2.8}$$

$$R = \frac{\Delta P}{\eta(T) \cdot J} \qquad (2.9)$$

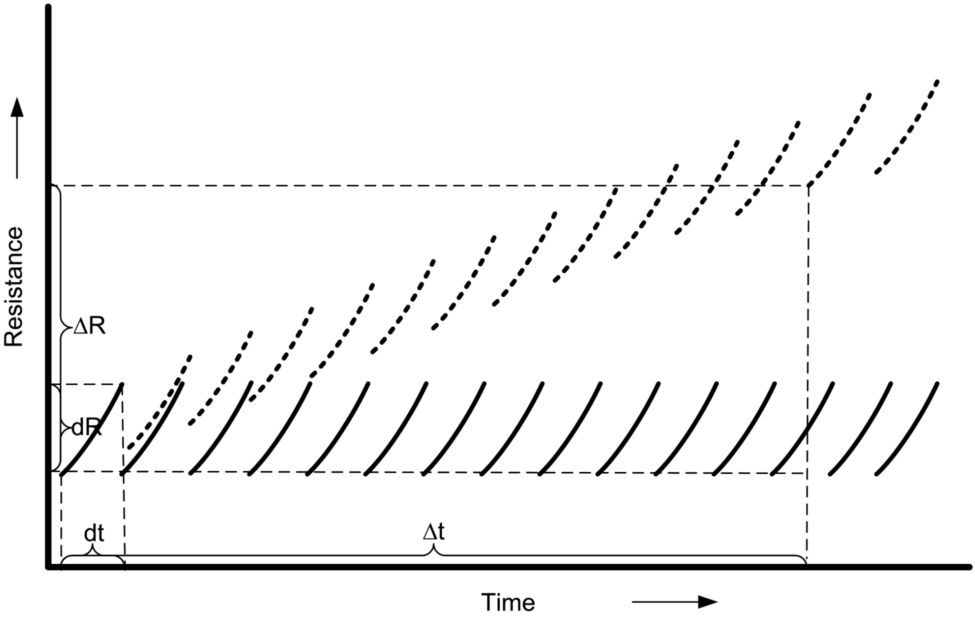

Figure 2.5 – Typical filtration curves illustrating filterability and reversibility

Reversibility is described as the extent within which the filtration resistance after applying a hydraulic cleaning is returned to the start value. If the filtration resistance after hydraulic cleaning is equal to the filtration resistance at the start of the previous filtration period, then the fouling is considered to be completely reversible (te Poele, 2005). Figure 2.5 shows two different filtration curves, with a different reversibility. The lowest filtration curve (covered line) is completely reversible. The reversibility can be determined after a few filtration periods and is illustrated in Figure 2.5 and described in equation 2.10.

$$\frac{\Delta R}{\Delta t} \qquad (2.10)$$

2.6 Summary

The conventional method for the treatment of municipal wastewater is the activated sludge process. After the treatment process the micro-organisms (activated sludge) are separated from the treated water (WWTP effluent) by sedimentation but the WWTP effluent still consists of different constituents that may foul the membranes when it is tertiary treated by e.g. ultrafiltration. In this thesis fouling is defined as "the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores".

In the literature soluble microbial products (SMP) and/or (soluble) extracellular polymeric substances (EPS) are considered as the major foulants of EfOM during ultrafiltration of WWTP effluent. But it has to be considered that in addition to soluble organic material, colloidal organic particles play an important role during ultrafiltration of effluent. With the analytical method that is mainly applied (specific UV-absorbance, total organic carbon, colorimetric analyses and size exclusion chromatography) only concentrations are characterized but not the size. Furthermore Roorda (2004) and te Poele (2005) have shown the importance of fractionation tests in order to quantify size of organic colloids. These studies have shown that especially the colloidal fraction of 0.1 – 0.2 µm causes fouling.

In order to remove fouling membranes are periodical chemically and hydraulically cleaned. In addition to these operational strategies the feedwater of membranes can also be pretreated. Main applied pretreatment technologies in practice are coagulation, prefiltration and adsorption. Unfortunately these pretreatment technologies do only partly remove the earlier mentioned fraction size of 0.1 – 0.2 µm. Therefore other pretreatment technologies have to be applied to remove this colloidal fraction. In the literature biofiltration (e.g. slow sand filtration) and the combination of coagulation – adsorption are considered as promising technologies. Therefore the performance of these technologies is investigated in the context of this thesis.

To measure the fouling rate/potential of WWTP effluent during ultrafiltration of WWTP effluent different methods are available. In this thesis the SUR measurement is used because the process conditions of this method are closely related to the process conditions applied in practice. Furthermore this measurement results in one value independent of the initial membrane resistance. On pilot and full scale the fouling is characterised in accordance to methods applied by other researchers.

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