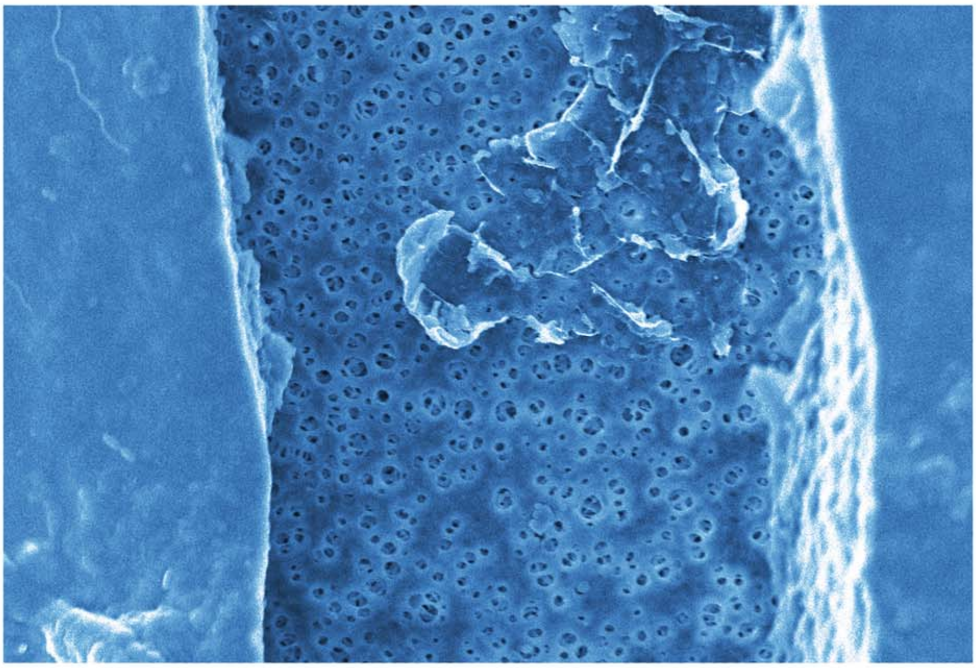
An integrated Membrane Bioreactor - Nanofiltration Concept with Concentrate Recirculation for Wastewater Treatment and Nutrient Recovery



Christina Kappel

AN INTEGRATED MEMBRANE BIOREACTOR – NANOFILTRATION CONCEPT WITH CONCENTRATE RECIRCULATION FOR WASTEWATER TREATMENT AND NUTRIENT RECOVERY

Christina Kappel

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AN INTEGRATED MEMBRANE BIOREACTOR – NANOFILTRATION CONCEPT WITH CONCENTRATE RECIRCULATION FOR WASTEWATER TREATMENT AND NUTRIENT RECOVERY

DISSERTATION

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1

General Introduction & Thesis Outline

Abstract

This thesis presents the opportunities and bottlenecks of an integrated MBR NF concept with NF concentrate recirculation to the MBR and integrated phosphorous recovery. The main aim of this MBR NF concept is reusable water production to encounter global water shortages. However, at the same time the concept allows the recovery of valuable nutrients. First, this introduction chapter gives an overview of the basic wastewater treatment concepts and shows where, why and how membrane systems are able to replace conventional processes. Improvement of water quality in any case goes along with a more challenging operational strategy when membranes are used. This part is followed by a description of the MBR NF process and emphasizes expected advantages and disadvantages. This introduction concludes with the outline of the following chapters of this thesis.

1.1 Water resources and usage

Water is a highly valuable resource. Statements have been made that in the future war might not only be fought over resources like oil, gold, money or personal freedom, but also over water [1]:

"If the wars of this century were fought over oil, the wars of the next century will be fought over water –unless we change our approach to managing this precious and vital resource"
- *Ismail Serageldin*

This very extreme statement inevitably shows that the availability and consequently the reuse of water become more and more important in the future, especially in regions where availability of fresh water is rare. Globally, only 0.3% of the water on planet earth is available as fresh water in lakes and rivers. A world average of 70% of that water is used for irrigation, the rest for domestic and industrial purposes [2]. Industrial use can be as high as 59% in high-income countries [3]. Reuse of water is therefore especially important for industrial applications and should become a main focus in the future. The reuse of process water is already handled on a larger scale. On the leading edge the Pearl GTL (gas to liquids) process from Shell in Qatar is designed to reuse as much as 45,000 m^3 of spent process water every day [4]. Such industry internal reuse decreases the overall environmental impact due to potential pollution, lowers the costs especially when fresh water prices increase and last but most important, decreases the overall fresh water demand. High water quality is especially important where direct contact of the reused water and humans, animals or plants occurs [5-7].

1.2 Membranes in municipal wastewater treatment

Sources for water reuse are not only effluents from industries, but also those from municipal wastewater treatment plants (WWTPs). Municipal effluents can be more easily reused and retransformed for instance into drinking water as their pollution is more straight forward and the type of pollution does not change dramatically over time. Also the pollution is usually not as hard to treat as that present in industrial wastewaters. Still, the contact of human beings with reused water from any type of wastewater faces psychological barriers and negative perception that make it difficult to introduce valuable water reuse concepts.

However, high quality municipal wastewater effluents can be obtained by upgrading conventional WWTPs with membrane technologies such as membrane bioreactors (MBRs) for secondary treatment as well as nanofiltration (NF) for tertiary polishing (Fig. 1.1). Those membrane concepts have the potential to deliver clean water that can be reused in agriculture, industry or sanitation and as such contribute to a sustainable global water supply.

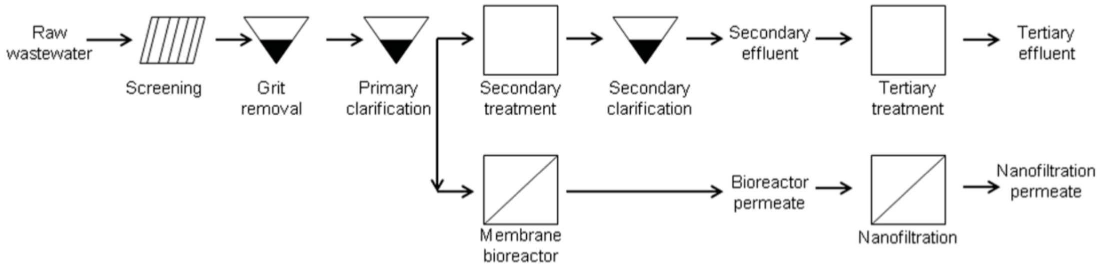

Fig. 1.1 *Conventional wastewater treatment stages and an alternative membrane-based process scheme.*

In a conventional treatment plant, the raw municipal wastewater (containing mainly e.g. proteins, carbohydrates, fats and oils as organic pollutants) first passes coarse screens (6-150 mm) to remove large floating objects, followed by a grit removal stage to separate heavier material (e.g. stones, metal) to protect further treatment stages [8]. After that the wastewater proceeds to the primary clarification stage. Here the first separation of suspended particles and water takes place. The water passes large circular or rectangular clarification tanks at low speed, giving the solids time to settle to achieve the separation. This primary treatment removes about 50-70% of the total suspended solids (TSS) and 25-40% of the biological oxygen demand (BOD) [8]. After the solids settled the remaining primary waste sludge, resulting from the primary clarification process, is further processed in sludge treatment facilities on site. The water itself proceeds through overflows to the secondary treatment stage. In this stage, conventional activated sludge (CAS) systems are commonly used. Different configurations are possible but the main targets are the removal of organic substances (quantified as chemical oxygen demand (COD) or biological oxygen demand (BOD)), as well as nutrient (N and P) removal. COD/BOD_5 removal is performed by heterotrophic bacterial community in the activated sludge. In the so-called aerobic stage in the secondary treatment, an aeration system supplies oxygen into the liquid via diffused-air or mechanical aerators. The presence of oxygen allows the bacteria to oxidize the organic material to CO_2 and water. Also nitrogen removal is performed in this secondary stage. The transformation of ammonium to nitrate (nitrification) by autotrophic nitrifiers (e.g. *Nitrosomonas*, *Nitrobacter*) is followed by an anaerobic (anoxic) process, where mainly heterotrophic bacteria reduce nitrate into N_2, which is released into the atmosphere. In addition to nitrogen, also phosphorous is removed in this secondary stage. This is done either chemically by precipitation, or biologically by enhanced biological phosphorous removal (EBPR). After the secondary stage, another clarification step is needed to separate the suspended solids (activated sludge) from the water. The settled sludge is (partly) recirculated back to the activated sludge tank. The waste sludge is treated further in the sludge treatment facility on site, where the sludge is dewatered. The clean water on the other hand slowly passes the large secondary clarification tanks and can either be discharged into the environment or can be polished further by tertiary treatment for water reuse. Besides the option of filtration that is elaborated on in this work, also adsorption, ion exchange as well as advanced oxidation processes [9, 10] can be used. Their use is very much dependent on the requirements and final reuse application of the water.

Membranes cannot only be applied in tertiary polishing, but also offer several advantages already in the secondary wastewater treatment stage. As shown in Figure 1.1, the secondary treatment (CAS) in the conventional process can be replaced by an MBR using porous low-pressure micro- or ultrafiltration membranes, while for the tertiary treatment and polishing step, NF can be applied. Figure 1.2 gives an overview of existing membrane types for water treatment and their corresponding rejection behavior of common pollutants.

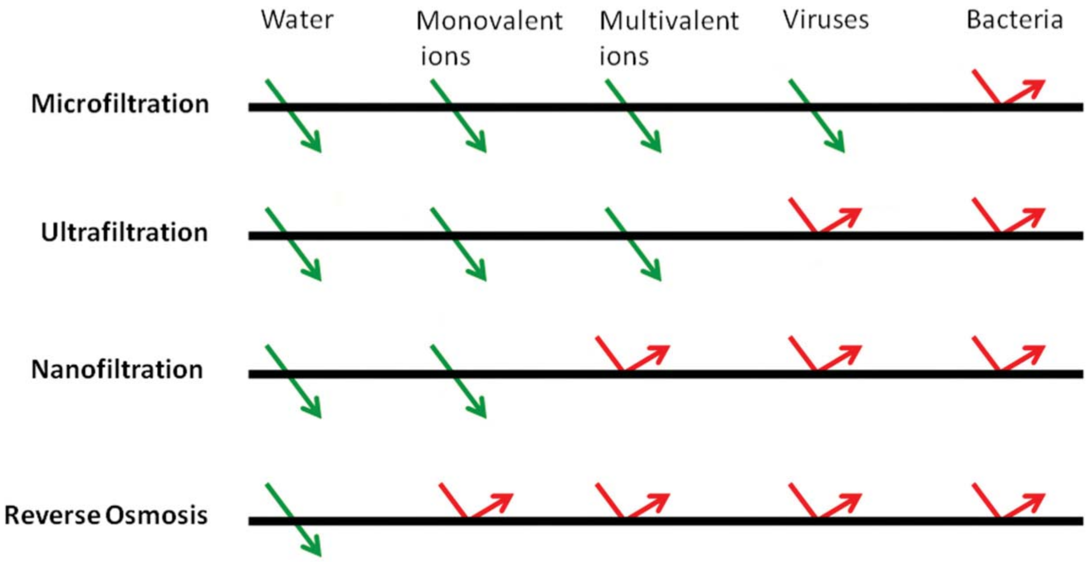

Fig. 1.2 *Overview of membrane separation processes and ranges of compound rejections (adapted from [11]).*

Open membranes categorized as microfiltration (MF)- or ultrafiltration (UF) membranes both reject bacteria, while UF membranes also retain viruses. Dense membranes like nanofiltration (NF) membranes reject bacteria, viruses and most multivalent ions. RO membranes even reject monovalent ions and all multivalent ions.

MBR technology combines microbiological treatment and membranes and mostly employs MF or UF membranes. An MBR consists of two compartments: a biology part and a subsequent membrane part. Both compartments are filled with sludge, where the sludge from the membrane compartment is continuously recirculated to the biology compartment and by that the sludge remains equally distributed. The separation of biology and membrane compartment allows different aeration systems and oxygen concentrations in both compartments. In the biology part, fine bubble aeration supplies oxygen for the bacteria necessary for the oxidation of substrates, while in the membrane compartment coarse bubble aeration is used to scour the MBR membrane surface to minimize membrane fouling. The membranes are in contact with the sludge but reject the sludge solids while the water permeates through the membranes. Additionally, anoxic or anaerobic biology tanks can be added for nitrogen and biological phosphorous removal.

The physical separation of sludge and water by the membranes in an MBR replaces the slow settling process in the secondary clarification occurring at low speed. As solids cannot pass the membranes, the water throughput can be much higher in an MBR, as the process becomes independent on the settleability of the sludge as is needed in a conventional system for good separation. The use of membranes allows the decoupling of the water throughput (HRT) and the residence time of the sludge solids (bacteria), i.e. solids or sludge retention time (SRT). This allows the treatment of higher wastewater loads in a shorter period of time. This additionally increases the sludge concentrations by physical separation as well as the supply of nutrients. This makes it possible for slow growing species, such as nitrifiers, to develop much more easily without being washed out of the system. Overall, the performance of the system especially in terms of nitrification is increased. As such, the MBR process is more resistant to disturbances like sudden changes in wastewater composition that can disturb the clarification process, while at the same time it has a higher treatment capacity and a smaller footprint compared to the large and slow conventional activated sludge system. Common sludge concentrations (MLSS, mixed liquor suspended solids) and hydraulic retention times for the conventional treatment system and an MBR are given in Table 1.1.

Table 1.1 *Typical sludge concentrations (MLSS) as well as solid (SRT) and hydraulic retention times (HRT) of a CAS and MBR process.*

		CAS	**MBR**
MLSS	**g L^{-1}**	1-3[b]	5-20[b]
HRT	**hrs**	4-8[b]	4-6[b]
SRT	**days**	5-15[a]	7-30[a]

a: [12]; b: [8]

As described, and MBR contains a biology and a membrane compartment and different MBR configurations can be used (Fig. 1.3).

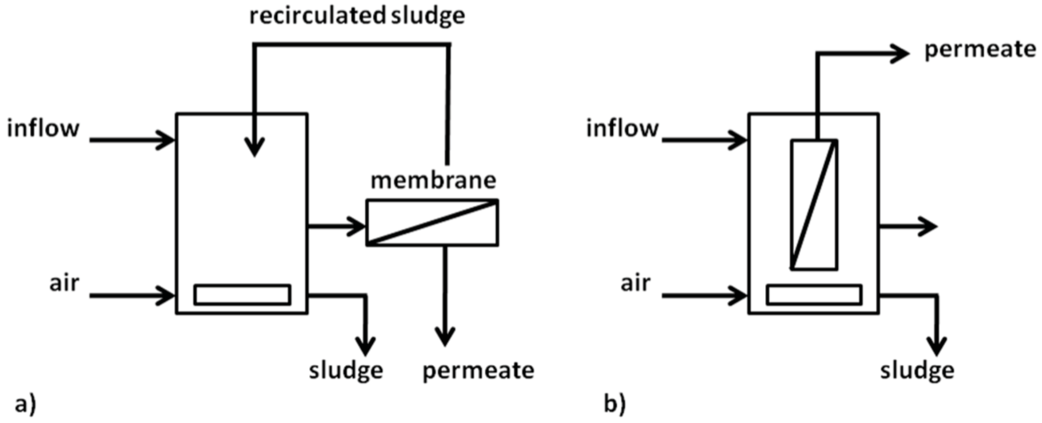

Fig. 1.3 *a) Side-stream MBR configuration and b) immersed MBR configuration (adapted from [12]).*

In the case of side-stream MBRs (Fig. 1.3a), the membranes are applied as external pressurized membrane modules. In a submerged MBR (Fig. 1.3b) the membranes are placed in the sludge and the permeate is extracted via suction. This allows different cleaning strategies, as in the case of side-stream MBRs the membranes can the cleaned in-place (CIP), while in a submerged unit the membranes need to be removed from the system for cleaning. Depending on the type of fouling, chemical cleaning agents (e.g. bases or acids) but also enzymatic cleaning agents are applied [13].

Besides chemical cleaning of the membranes, also relaxation steps are applied in an MBR. During this relaxation step, permeate extraction is stopped. This relaxation step decreases the drag force towards the fouling layer of the MBR membranes and air scouring can remove some of the less compact fouling. This can be done for instance in continuous cycles of 8 minutes filtration followed by 2 minutes relaxation [12].

The micro- or ultrafiltration membranes in an MBR are available in different configurations, i.e. as flat-sheets (plate and frame), hollow fibers (outside-in) and (multi)tubular (inside-out) and can be made from different materials (metallic, ceramic or polymeric) [12]. All configurations retain the solids that are present in the reactor and as such, all MBR permeates are solids-free. This makes MBR permeates very valuable for further water reuse [14, 15]. However, to facilitate reuse of the MBR permeate, tertiary treatment is still necessary to remove recalcitrant compounds like viruses, endotoxins, pesticides, hormones, micropollutants or heavy metals.

1.3 Nanofiltration permeate: a source for water reuse

Dense high-pressure membrane processes like nanofiltration (NF) and reverse osmosis (RO) (Fig. 1.2) are excellent technologies for tertiary treatment of MBR permeates, as they both deliver very high quality water. Nevertheless, for many applications the very high energy demand of RO membranes is a major bottleneck. Even though NF permeate still contains monovalent ions unlike RO permeate, the very good quality of the NF permeate and the lower required pressures (and as such lower energy consumption) make NF attractive for water reuse purposes.

Nanofiltration uses membranes that have a molecular weight cutoff (MWCO) of approximately 150-300 Dalton [8, 16]. The physico-chemical filtration (separation) mechanisms of NF are based on sorption-diffusion, convection or Donnan exclusion. These lead to the efficient retention of most recalcitrant target contaminants present in the MBR permeate, like inorganics (multivalent ions e.g. phosphates), residual organics [17, 18] as well as all coliforms (bacteria) [19]. The water obtained after the suggested MBR NF process could be reused in different sectors for e.g. agriculture, irrigation of sports grounds, urban and industrial use as well as for aquifer recharge [20, 21]. Also recreational and environmental as well as potable and non-potable urban reuse are possible [22]. Nevertheless, the water quality required for reuse is very much dependent on the specific reuse application.

The legislation for water reuse differs within the EU countries and is additionally dependent on the reuse application, but also on the water source itself. Some more specific regulations as imposed in the U.S. can already be achieved by the MBR process alone. An example is the turbidity, which is (with a value of 1 NTU in the MBR permeate) already below the limit required in the United States [8]. Especially direct or indirect biological contamination by microorganisms or viruses is a potential health risk when humans come into contact with raw sewage. The U.S. EPA regulates coliforms (0 in 100 mL), but also BOD (≤ 10 mg L^{-1}), turbidity (≤ 2 NTU) and chlorine residuals (1 mg L^{-1}) for water reuse [8]. Bacterial contamination can mostly be prevented by MBR technology and full prevention including viruses is possible when the MBR is combined with a tertiary NF [23]. The NF permeate meets the restrictions of coliforms (0 in 100 mL) for unrestricted urban use, agricultural reuse (food crops not commercially processed), recreational impoundment and indirect potable reuse [24]. Further limitations for water reuse in e.g. irrigation are trace elements, chlorine residuals as well as nutrients like nitrogen, phosphates or potassium. These are regulated to avoid eutrophication of the environment and to reduce the oxidation potential. Also the removal of trace organic matter such as for example carboxylic acids or aromatic organic compounds is important [21]. Very high membrane rejections are needed to remove trace contaminants, especially when indirect potable reuse is considered. To reach such very high rejections, the type of trace contaminant and the type of nanofiltration membranes used are determining [25, 26].

In countries where water containing nutrients from wastewater can be used as fertilizers, the application of these waters is still dependent on the type of plants that are irrigated, as already mentioned before [27]. A study showed that the irrigation of soil with untreated secondary wastewater effluents caused accumulation of recalcitrant organic compounds like polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and phenols in plants grown on this soil [28]. Reclaimed water from oxidation ponds for example can still contain heavy metals and micropollutants, which may also become an issue when MBR permeate is used. Those compounds become a major concern when they accumulate in soil over a longer period of time [29]. Also the salinity is a very important factor when water reuse is considered. Here the differences in salt rejection of NF and RO membranes can be significant. However, the salinity acceptable for reuse again depends on the specific soil and the capability of the specific plants to cope with high saline waters [30]. As NF is less efficient in decreasing the salinity than RO, this should be considered when selecting the type of membrane for tertiary treatment.

The examples described above show that water reuse from wastewater treatment plants has to be evaluated carefully in terms of feed, legislation and final application, and that source oriented tertiary treatment systems are needed.

1.4 The MBR NF process

As described above, the MBR NF process combines two types of membranes, where the MBR can be considered as the first stage with its permeate serving as feed for the subsequent NF, with the overall aim of water reuse. The MBR not only decreases conventional wastewater characteristics such as COD, BOD, nitrogen and phosphorous, but can also adsorb micropollutants, which finally end up in the waste sludge. The subsequent NF removes most of the inorganic contaminants but also the remaining micropollutants (small organics) and multivalent ions that were not addressed in the MBR. The NF performance is highly determined by the quality of the MBR operation at front, and so is the quality of the final NF permeate for water reuse.

As for all membrane processes, the main bottleneck of the NF operation is the generation of a highly concentrated retentate stream. As it originates from wastewater, this stream may be highly contaminated by for instance hardly biodegradable compounds (especially by harmful endocrine disruptors), which limits the possibilities for direct discharge to the environment.

Common disposal methods for NF concentrates are evaporation, dumping in landfills or discharge to sewers or surface and groundwater. However, this discharge can cause damages to the environment [31]. Contradictory to this, NF concentrates are an excellent source for the recovery of valuable nutrients (e.g. phosphorous), which suggests much more sustainable treatment alternatives [32].

1.5 Concentrate recirculation

Decreasing the discharge of NF concentrate and increasing the recovery of valuable nutrients from the concentrated NF retentate stream is of major importance for obtaining a sustainable process [33, 34]. One approach to achieve this is the recirculation of the NF concentrate back to the MBR (Fig. 1.4) [35, 36]. Prior to concentrate recirculation, valuable components can be recovered from the NF concentrate.

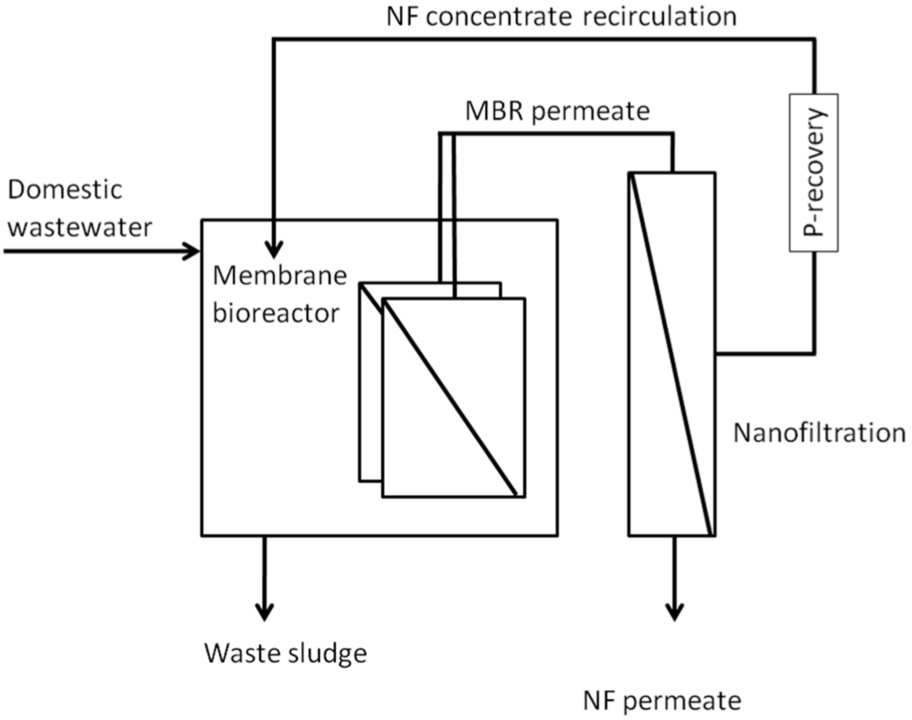

Fig. 1.4 *Scheme of an integrated MBR NF process including concentrate recirculation and a recovery stage for phosphorous.*

In principle, concentrate recirculation returns all components rejected by the NF (mainly viruses, divalent ions and dissolved organics, see Fig. 1.2) to the MBR. Next to the wastewater, the MBR in such a recirculation process receives an additional NF concentrate stream to be treated. This recirculation increases the residence time of the compounds, which may improve their biodegradation. In literature the recirculation of part of an RO concentrate was mentioned to increase biomass concentrations due to increased organic carbon mass removal from the RO concentrate [37]. Generally, if no conventional phosphorous removal is performed, recirculation also increases the concentrations of e.g. phosphorous, which could be recovered and reused [32]. An additional advantage is that the recirculation of divalent ions, especially when nanofiltration concentrate is considered, can support the bioflocculation process as divalent ions (calcium and magnesium) are known to bind negatively charged extracellular polymeric substances excreted by the bacteria [38]. This improved bioflocculation may as well improve the filterability of the sludge. However, at the same time recirculation may decrease the separation performance of the membranes due to the increased load. Finally, recirculation may also have consequences for the biology in the MBR as it can influence or change the microbiological community by increased heavy metal concentrations. Also the sludge treatment may be affected, e.g. anaerobic digestion, dewatering or thickening.

The consequences, advantages and disadvantages of an integrated MBR NF concept with concentrate recirculation are presented and discussed in this thesis.

1.6 Outline of the thesis

NF concentrates, resulting from reusable water production with an MBR NF process, can have a negative impact on the environment if they are simply dumped and not treated properly. To not only minimize the environmental issues but also to investigate a more sophisticated treatment route for the production of reusable water, including nutrient recovery and reduction of waste streams, the recirculation of NF concentrates to the prior MBR is examined experimentally and the possible impacts in terms of biology and membrane operation are evaluated and discussed. Also, the opportunity of recovering valuable phosphorous is presented.

Following this introduction chapter, the major characteristics, advantages and disadvantages of an MBR NF process are discussed and presented in this thesis:

Chapter 2: ***Membrane bioreactor and tertiary nanofiltration (MBR NF) for water reuse: A review***

This chapter summarizes the main literature on MBR NF concepts. The chapter discusses factors determining the operation of this combined membrane system, as well as its capabilities and performances. Though, literature focusing especially on NF concentrate recirculation within the MBR NF process is not extensive. Therefore, besides an insight into the existing field, this review also highlights new challenges and opportunities regarding NF concentrate recirculation.

Chapter 3: ***Effects of nanofiltration concentrate recirculation on membrane bioreactor performance***

This chapter discusses the influences of NF concentrate recirculation, especially focusing on the MBR biology. General treatment performance, such as removal of COD/BOD and nitrification, are presented and compared for two reactors operating over 200 days; one with and one without NF concentrate recirculation. Following a COD mass balance the mineralization and sludge production are presented and changes due to the recirculation in floc strength, sludge morphology, elemental sludge content as well as bacterial respiration are shown. From this, the impact of concentrate recirculation on the biological MBR performance is addressed.

Chapter 4: ***Impacts of NF concentrate recirculation on membrane performance in an integrated MBR and NF membrane process for wastewater treatment***

The effects of NF concentrate recirculation on the membrane performance and fouling behavior of the MBR as well as the NF membranes are experimentally investigated and evaluated in this chapter. Results from a continuously performing MBR NF setup (over 200 days) are presented. For a more detailed investigation, results from additional filtration tests in comparison with a blank reactor are shown and finally also membrane autopsies are included in the evaluation. This altogether presents the main causes for fouling in the integrated concept, especially pointing out the main bottlenecks of MBR NF.

Chapter 5: ***Electrochemical phosphate recovery from nanofiltration concentrates***

Calcium phosphate scaling was pointed out as a major issue in the MBR NF concept. Nevertheless, this also strongly emphasizes the availability of valuable phosphorous. Therefore, integrating a phosphorous recovery step could not only aid the operation but also recover this rare nutrient. In this chapter an electrochemical recovery technique for phosphorous from NF concentrate is presented. Results of the recovery as a function of applied voltage and pH, as well as the analyses of the precipitates are presented in this chapter. This approach for phosphorous recovery could potentially be integrated in the MBR NF process for continuous phosphorous recovery in the form of amorphous calcium phosphates.

Chapter 6: ***Performance of an MBR NF process for wastewater treatment with NF concentrate recirculation and integrated phosphorous recovery***

The implementation of a phosphorous recovery step into an MBR NF system and the following consequences for mainly the membrane operation are elaborated on in this final experimental chapter. The impact of the phosphorous recovery step on MBR and NF membrane operation are evaluated and the results are compared to those obtained with a single MBR reactor neither with any NF concentrate recirculation nor phosphorous recovery. Additional filtration allows a detailed evaluation of the NF resistances with changing phosphorous content in the three reactor systems. These results show the potential of this integrated MBR NF concept with concentrate recirculation for waste treatment that allows the production of reusable water while at the same time provides a source for valuable phosphorous recovery.

Chapter 7: ***General conclusions & outlook***

With the support of the earlier investigations, this chapter reveals the final conclusions of the results described in this thesis and addresses the overall feasibility of the MBR NF process. Additionally, future research opportunities regarding the integration of phosphorous recovery and separation in the MBR NF process are discussed. Also impacts on sludge treatment, micropollutants as well as possibilities for reusable water production and concentrate treatment with MBR NF are discussed.

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2

Literature review: MBR NF

Abstract

This chapter summarizes the literature on MBR NF processes and reflects on the potential opportunities and challenges. First the different factors that can impact the MBR NF operation are discussed. Subsequently, the performance and capabilities of the MBR NF system as obtained from literature are presented. As most literature focuses on micropollutants, the removal of these in an MBR NF processes is specifically addressed. Additionally cleaning strategies for MBR as well as NF membranes found in MBR NF applications are presented as well. Only a small number of papers specifically focus on MBR NF systems with NF concentrate recirculation and the results of these papers are discussed in terms of the influence of the recirculation on the performance of the process. As MBR NF processes with concentrate recirculation are mostly considered to treat highly polluted streams (mostly treating accumulated organics), often, additional oxidation or adsorption steps are required and those are presented as well. The chapter ends with some concluding remarks and perspectives.

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2.1. Introduction

Nowadays, water scarcity is the main driver for water reuse from wastewater. Domestic, but also industrial wastewaters are largely available. If treated with the appropriate technology, these can be transformed into valuable process-, irrigation-, ground- or surface water, and can even be a source for potable water production. Technologies for the production of reusable water do not only dependent on the type of wastewater but also on the targeted compounds as well as on the field of application of the reclaimed water. This together also determines the targeted effluent quality.

Besides tertiary treatment like constructed wetlands, enhanced clarification or sand filters, also dense membrane processes can be applied to effectively and reliably remove most targeted compounds from wastewaters and at the same time deliver very high permeate quality for water reuse. Even smaller compounds like micropollutants (e.g. endocrine disrupting compounds (EDCs), pharmaceutically active compounds (PhACs), or personal care products) can be rejected to a large extend.

The main bottleneck of these membrane processes is the production of a concentrate stream. Discharge of membrane concentrates can be environmentally harmful as they contain high salt concentrations as well as rejected micropollutants and regulations exist to control the discharge of such concentrated waste streams.

A sustainable solution to produce high quality reusable water and at the same time decrease concentrate discharge is the combination of a micro (MF)- or ultrafiltration (UF) based membrane bioreactor (MBR) followed by a subsequent pressure driven dense membrane process like nanofiltration (NF) or reverse osmosis (RO), with integrated concentrate recirculation to recirculate the NF or RO concentrate back to the MBR. This process was first patented in 1992 by the Wehle-Werk AG [1] and published in 1994 as BioMembrat-Plus® [2]. This concept forces the use of NF rather than RO as RO produces highly saline concentrates. When fully recirculated back to the MBR, this highly saline RO concentrate would effectively increase the osmotic pressure on the bacterial cells in the MBR and dramatically diminish the biological activity in the MBR [3]. This review therefore focuses on the combination of MBR and NF processes only (Fig. 2.1).

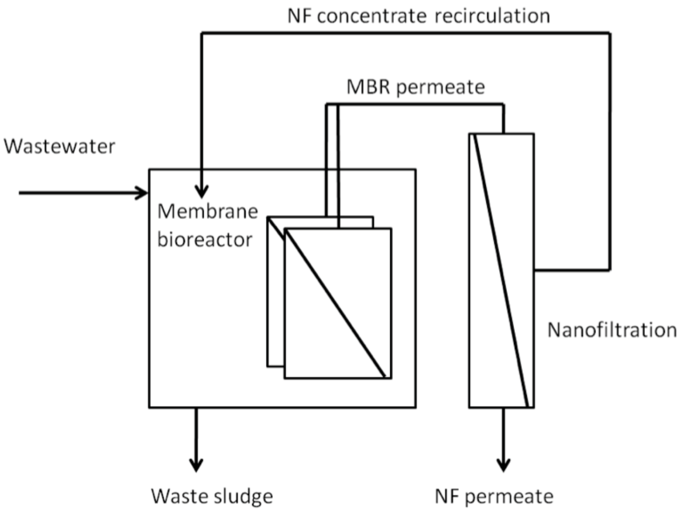

Fig. 2.1 *Overview of MBR NF treatment scheme with NF concentrate recirculation.*

An MBR can treat different types of wastewater: municipal, domestic or industrial. The biologically sensitive compounds (e.g. micropollutants that are biologically sensitive, COD) are degraded by the biological sludge in the MBR. Subsequently the aqueous phase is separated from the sludge by an MF or UF membrane in the MBR. This MBR permeate is further polished by an NF membrane process to allow water reuse. The NF membrane has a distinctively smaller pore size than the MF or UF membrane in the MBR, and therefore an increased retention of smaller components. NF has a great potential for the removal of micropollutants as well. The MF or UF membranes in the MBR retain bacteria as well as relatively smaller molecular weight organics and deliver a solids free permeate with reduced (bio)fouling potential compared to effluent from conventional settlers [4]. Wastewater treatment by MBRs therefore ensures a higher productivity of the tertiary NF membrane compared to the effluent from conventional activated sludge processes that might as well contain solids when the settling process is disturbed.

Literature shows a number of papers reporting the combination of MBR NF. Not all papers however actively take the MBR operation into account, but only consider the MBR operation using spiked MBR effluent (mostly an organics containing matrix). Only few papers focus on the further processing of the concentrate that is produced and consider NF concentrate recirculation back to the MBR.

This chapter summarizes the literature on MBR NF processes as schematically depicted in Fig. 2.1. A summary of the impact of membrane properties and feed water matrix on the MBR NF operation and more specifically the removal of certain components is presented. Membrane fouling and cleaning strategies are highlighted and general performance in terms of COD removal and nitrification, color and most extensively the ability the removal micropollutants is discussed. As the removal of micropollutants is especially important when water is reused for instance for drinking water production, the removal of such micropollutants in an MBR NF processes is specifically addressed. Additionally cleaning strategies for MBR as well as NF membranes found in MBR NF applications are presented. Finally, the limited literature on the implementation of a concentrate recirculation in MBR NF is presented. As MBR NF processes with concentrate recirculation are mostly considered to treat highly polluted streams (mostly treating accumulated organics), often additional oxidation or adsorption steps are required and those are presented as well.

2.2. Theoretical background

2.2.1 Introduction

This paragraph summarizes the main parameters commonly used to assess MBR NF process performance and to compare different MBR NF applications. The first part will address the most important membrane related parameters, while the second part is dedicated towards solution and component properties.

2.2.2 Membrane theory

The flux J of a membrane describes the water that permeates the membrane in a certain amount of time (s^{-1}) per membrane area (m^2). The flux can be calculated by dividing the permeate flow Q_{per} ($m^3\ s^{-1}$) by the area of the membrane A_{mem} (m^2) [5]:

$$J = \frac{Q}{A_{mem}}$$

To achieve water permeation across a membrane, a certain driving force is needed. Driving forces can be for instance a pressure gradient (ΔP) or a salt gradient. Open membranes such as micro- or ultrafiltration membranes require lower driving forces, mainly due to the larger pore size and therefore lower membrane resistance compared to NF and RO membranes. Membranes can be operated in a constant pressure or constant flux mode.

The performance of the membrane for an aqueous feed in the absence of any solutes (e.g. salts, organics or bacteria) at a certain pressure is defined as the clean water flux. As soon as contamination in the aqueous phase is present, also several other resistances (i.e. concentration polarization, adsorption, pore blocking, cake, gel or biofilm resistances) start to play a role and can increase the total resistance R_{tot}. Concentration polarization can decrease the membrane flux (increase resistance) for instance in ultrafiltration as it can lead to gel-layer formation causing additional resistance to filtration. In NF and RO concentration polarization can lead to decreased salt rejections or even scaling at the membrane surface. Additionally, concentration polarization causes increased osmotic pressures. The membrane flux J ($m^3\ m^{-2}\ s^{-1}$) can be calculated as follows [5, 6]:

$$J = \frac{\Delta P}{\left(\mu \cdot R_{tot}\right)} = \frac{\left(TMP - \Delta\pi\right)}{\left(\mu \cdot \left(R_{mem} + R_{fouling}\right)\right)}$$

with

ΔP	pressure gradient (Pa)
μ	dynamic permeate viscosity at 20 °C (Pa s)
R_{tot}	total resistance (m^{-1})
TMP	transmembrane pressure (Pa)
$\Delta\pi$	osmotic pressure (Pa)
R_{mem}	membrane resistance (m^{-1})
$R_{fouling}$	fouling resistances (m^{-1})

To account for the applied driving force, i.e. pressure gradient, the flux can be divided by the pressure difference over the membrane, giving the permeability.

The rejection R (%) of a membrane for a specific compound can be calculated [6] by:

$$R = 1 - \left(\frac{C_{per}}{C_{feed}}\right) \cdot 100\%$$

with

C_{per}	permeate concentration (mol L^{-1})
C_{feed}	feed concentration (mol L^{-1})

Especially during batch filtration (for instance in an Amicon cell) a certain feed water volume is concentrated at the feed side. The volume reduction factor VRF [6], also known as the concentration factor CF (-), between the feed and the concentrate is calculated by:

$$CF = VRF = \frac{V_{feed}}{\left(V_{feed} - V_{per}\right)} = \frac{V_{feed}}{V_{conc}}$$

with

V_{feed}	starting volume of the feed (m^3)
V_{per}	permeated volume (m^3)
V_{conc}	concentrate volume (m^3)

A certain amount of feed water is recovered as permeate, that can be reused. The water recovery (%) is defined as:

$$\textbf{Recovery} = \frac{V_{per}}{V_{feed}} \cdot 100\%$$

2.2.3 Solution and component properties

Hydrophobicity defines the aversion of a compound or surface for water, hydrophobic compounds therefore tend to avoid water, whereas hydrophilic compounds are “attracted” by water. Hydrophobicity or hydrophilicity can be defined by the partition coefficient log P (P = ratio of compound found in octanol and water) or log K_{ow} (octanol water coefficient), the logarithm of the partition coefficient between octanol (organic phase) and water of a neutral compound at a specific pH. This log K_{ow} value can be extended to a log D (distribution) value, which also applies to charged species. Therefore, log D is a measure for especially the hydrophobicity or hydrophilicity of negatively or positively charged components [7]:

$$\text{(negatively charged)} \qquad \log D = \log K_{ow} - \log(1+10^{(pH-pKa)})$$
$$\text{(positively charged)} \qquad \log D = \log K_{ow} - \log(1+10^{(pKa-pH)})$$

Components with log D > 3.2 are considered as hydrophobic, whereas those with log D < 3.2 as hydrophilic [3]. Neutral compounds have a high log D value and dissociated compounds a lower one. Log D values are reported for instance for several micropollutants, which help to estimate their behavior in the presence of a typical hydrophobic or hydrophilic surface (e.g. membrane). In MBR NF research hydrophobicity of a component (of e.g. micropollutants) is used to explain the rejection behavior and the interaction with the membrane surface.

Additionally, a solution can be analyzed in terms of aromaticity of organics, which can also be used as an estimation for hydrophobicity. This aromaticity is determined by measuring the specific ultraviolet absorbance (SUVA, L mg^{-1} m^{-1}). The SUVA is calculated by dividing the UV absorbance (at 254 nm) by the dissolved organic carbon concentration of the sample:

$$\mathbf{SUVA = UV / DOC}$$

with

UV = absorbance at 254 nm (expressed in m^{-1})
DOC = dissolved organic carbon (mg L^{-1})

With a SUVA value > 4, the water is high in aromatic organics and can be considered aromatic and hydrophobic in nature, whereas at SUVA values < 2.5, the water is considered to be highly hydrophilic [8, 9].

Finally also the zeta-potential is an important parameter that indicates the surface charge of a membrane or colloids in a water phase. The zeta-potential is the potential in the electrical double layer at a solid-water interface. It is the electrostatic potential of the shear plane between stern layer and liquid phase [10]. The zeta-potential provides information about the charge of a clean membrane but also of that of a fouled one. This can for instance help to evaluate the fouling potential of a feed solution or it can be used to identify the nature of a fouling layer.

2.3 What determines the performance of MBR NF?

2.3.1 Introduction

When the production of reusable water with an MBR NF concept is considered, next to the removal of e.g. inorganics (salts) and organics (e.g. humic acids), especially the removal of micropollutants is a great challenge as these are hardly removable by conventional wastewater treatment processes. Several parameters determine the removal efficacy of such components, as will be discussed below. Those parameters are related to the compound itself, but also the membrane (MBR and NF) and the feed water matrix (of the wastewater in the case of the MBR, and of the MBR permeate in case of the NF) [11]. It is difficult to distinguish between the effect of the characteristics of the compound, the membrane and the surrounding solution matrix on the removal efficacy, as these parameters all interact simultaneously. These different parameters and their interactions are presented in the following paragraphs. As most of the MBR NF literature focuses on micropollutant removal, the overview mostly focuses on the treatment of micropollutants, also referred to as “target compound”.

2.3.2 Component properties

The characteristics of the target components in the wastewater (e.g. micropollutants) are very diverse. The most obvious characteristic of a compound is its **size** i.e. the molecular weight (MW). Common micropollutants have a molecular weight in the range of 100 Da (e.g. Chloroform, 119.38 Da) to 296 Da (Diclofenac), but can be as high as 491 Da (Glimepiride) or even > 600 Da (diatrizoates) [12]. Rejection by size is also known as molecular sieving, and is especially important when porous membranes like MF or UF are used. However, molecular sieving is also assumed to play a role when NF membranes are considered [13].

Also the **hydrophobicity** of the target compounds plays a role and hydrophobic interactions were mentioned in literature as a possible rejection mechanism [14]. A general trend in rejection behavior in relation to hydrophobicity was found in MBR NF operation: the MBR mainly removes hydrophobic compounds (log D > 3.2) as those adsorb to the sludge flocs, whereas removal of hydrophilic compounds (log D < 3.2) by the MBR is much lower. Those hydrophilic compounds are subsequently rejected to a large extend by the NF [15-17]. Additionally, hydrophobic compounds can also be removed by for instance by precipitation or adsorption [3]. However, some hydrophobic compounds (e.g. t-octylphenol) do pass the MBR and can hardly be removed by NF and are even detectable in RO permeate [17].

Hydrophilic compounds are hardly removed by the MBR. A great range of compounds with a variety of different characteristics (log D, size, charge, structure, etc.) can be present in the wastewater. Hydrophobicity for example can range from very low log D values (salicylic acid: 1.13) up to high log D values (4-n-nonylphenol: 6.14). This clearly suggests that hybrid processes are essential to address all compounds with one treatment train.

Another important compound characteristic is the **dissociation constant (pKa)**, which provides information about the charge of a molecule at a specific pH. The resulting charge of the molecule for instance contributes to its rejection or adsorption. If a compound is for instance positively charged purely based on charge, it will not be rejected by a negatively charged NF membrane, compared to when negatively charged compounds are considered. Again, the range of pKa values of components in wastewater is very broad. For example, micropollutants with pKa values ranging from -1 (DEET) up to 15 (diclofenac) have been identified [17], which makes it difficult to address all compounds in one single treatment step. Obviously, also anions and cations present in the solution are of great importance.

The mechanism for rejection of a compound based on charge is called **electrostatic repulsion**, which takes place when a charged membrane surface rejects a similarly charged compound or ion. In literature, electrostatic repulsion is suggested as a dominant rejection mechanism for negatively charged compounds in an NF [16] as NF membranes are usually negatively charged at neutral solution pH. Charge interaction between NF and target compound also plays a role regarding the rejection of e.g. negatively charged NOM or even bacterial cell walls. Neutral compounds such as carbamazepine in comparison have a relatively low rejection by NF [18]. Charge therefore is an important compound characteristic. The higher the charge density of a compound, generally speaking, the higher the rejection can be (as a consequence of electrostatic repulsion). Of course the actual rejection in a practical application not only depends on the charge but also on the other different characteristics, as described.

Next to electrostatic repulsion, also **adsorption** plays a role when discussing target compound removal. Adsorption can be very important when for instance micropollutants are not rejected by the MF or UF membrane in the MBR, simply because they are too small in size (much smaller than the pore size or MF or UF). However, in case they are bound to the sludge in the MBR via adsorption, they can be rejected by membranes with much bigger pore sizes than the actual size of the specific compound itself [19]. Depending on the specific properties (e.g. charge, hydrophobicity) of the specific compound and of the membrane, also adsorption to the NF or MBR membrane can occur, resulting in fouling of the membrane.

The **solubility** (associated to the hydrophobicity) of a compound in the wastewater also contributes to the behavior of that specific compound in the MBR NF process. In general, highly soluble compounds show lower adsorption to e.g. the membrane surface, and the compound can permeate the membrane more easily [20]. Furthermore **polarity** (dipole moment) [21, 22] of a compound was shown to decrease the rejection of a compound by an NF membrane, as the dipole can be directed towards the membrane surface and by that the electrostatic repulsion is decreased.

The **biodegradability** of a component is important when regarding the treatment by the MBR [15]. Biodegradation can be enhanced by prolonged retention times via adsorption of for instance micropollutants to the sludge. This not only contributes to the overall removal, but also additional biodegradation may occur due to the longer contact time between the compound and the biology in the MBR (also dependent on the sludge retention time (SRT)). In literature it was mentioned that e.g. bisphenol A (BPA) removal is attributed to biological degradation at long SRTs [22]. Also longer hydraulic retention times aid the removal of for instance macrolides (a group of drugs containing a macrolide ring) by the MBR. Removal of for example azithromycin was highest (70-80%) at an HRT of 16 hrs, whereas at an HRT of 4 hours the removal was only 10-20% [19]. This was related to the retention time inside the reactor, and therefore to the association of azithromycin to the sludge and additional biodegradation. The same was observed in a different type of bioreactor (moving bed biofilm reactor, MBBR) for the degradation of oily compounds in bilge water (shipboard wastewater). Higher HRT resulted in increased removal percentages [23]. One of the envisaged advantages of an MBR NF process with NF concentrate recirculation is the foreseen longer retention times for compounds that are difficult to digest. Additionally, it was found that biological degradation is less effective when components contain high electron withdrawing functional groups (such as chlorides, amides) that hinder the oxidative catabolism of those components [24]. Compounds containing such groups are for instance micropollutants such as diclofenac or carbamazepine, which explains their low removal by MBR. The latter one could only be removed up to 30% in an MBR process [15].

Removal percentages and mass balances indicate that for some pollutants also the occurrence of stripping due to biological and/or membrane aeration has to be considered, especially when the component is highly **volatile**. High volatility is related to high Henry constants [24], which give the partitioning between the gas and the liquid phase. Volatility is especially important when toxic compounds (acrylonitrile –butadiene-styrene present in petrochemical wastewater [25]) are regarded as these should not end up in the atmosphere.

2.3.3 Membrane properties

The properties of the constituents in the feed usually determine the choice for a specific treatment process. In case of a membrane system, also the properties of the membrane play a dominant role in terms of water production and purity. Relevant membrane properties of importance for flux and rejection performance are discussed below.

One of the most often parameters to characterize (porous) membranes is the **molecular weight cutoff (MWCO)** [18]. The MWCO is not a physical parameter (that would be the pore size itself) but a characteristic of the membrane in relation to the feed. It refers to that specific molecular weight of a molecule that is 90% retained by the membrane. Compounds with a molecular weight below this cut-off value will pass the membrane, compounds with a molecular weight above the MWCO will be retained to a large extent. Following [12, 26], the different membrane types can be characterized in terms of their MWCO: MF (1,000,000 – 250,000 Da) and UF (250,000-5,000 Da) only reject high molecular substances and e.g. bacteria and viruses, whereas NF (5,000 – 250 Da) and RO (<250 Da) reject low molecular components and multi- and monovalent (RO) ions

In an MBR NF process, a variety of NF membranes with different salt retention characteristics can be selected for tertiary treatment of the MBR permeate, depending on the requirements of the final product. A tighter NF membrane may exhibit higher retention characteristics, but at the same time flux will be lower and fouling and scaling may be more severe [27]..

A comparison of a tight ($CaCl_2$ retention: 40-60%) and a more open ($CaCl_2$ retention: 85-95%) NF membrane [6] revealed that the tight NF membrane repelled organics (aldehydes, carboxylic acids, esters and nitrites) for more than 90%. In contrast, the more open NF was only able to reject the latter compounds at a rejection of < 50% only.

The **charge** of the membrane is important since interaction (either rejection or attraction) between the membrane and the components based on charge (electrostatic repulsion) may occur, as mentioned before. However, e.g. negatively charged membranes and negatively charged components (humics, NOM) can also be bridged by divalent cations (e.g. Ca^{2+}) present in the wastewater. This might increase component retention but additionally form a dense fouling layer on the membrane surface [28].

Not only hydrophobicity of the components plays a role as highlighted before, but also that of the membrane. Membrane **hydrophobicity** is measured as **contact angle.** A higher contact angle (above 90°) indicates higher hydrophobicity of the membrane surface. Increased hydrophobicity of the membrane was found to increase the retention of some endocrine disrupting compounds (EDCs) [22] but also resulted in lower permeabilities. More hydrophilic membranes on the other hand are more water permeable [22, 29, 30]. Despite the properties of the native membrane, membrane fouling can completely change RO or NF surface characteristics. The formation of a fouling layer (cake or gel) can lead to increased concentration polarization and increased surface roughness, both causing increased flux decline in time on the NF [17]. Additionally, not only the feed water but also the imposed cleaning strategy can significantly impact the membrane surface properties (e.g. hydrophobicity). For instance the surface hydrophobicity of an NF270 (DOW) membrane surface was decreased after use of a series of different caustic cleaning agents, resulting in an increase in permeability but a decrease in rejection of trace organic compounds (pharmaceuticals) [31]. Most MBR membranes have hydrophilic surface characteristics, to allow a high water flux [32].

Finally the **mode of operation**, i.e. cross flow or dead-end, can influence the rejection. Switching from dead-end filtration to cross flow filtration increases the convection at the membrane surface (force away from the membrane) and improves mixing and reduces concentration polarization at the membrane surface, resulting in higher rejections [33].

2.3.4 Feed water matrix

Wastewater is a complex multicomponent mixture and the different components in the wastewater show a wide diversity in their properties (e.g. component chemistry, molecular weight, hydrophobicity, charge). Different components can show mutual interactions and as such a mixture of components can show different behavior in terms of membrane performance than the individual components. Often wastewater contains natural organic matter, besides the components of main concern, such as heavy metals or micropollutants. Adsorption of micropollutants onto natural organic matter present in wastewater can increase micropollutant rejection for instance due to the larger macromolecular size of the associated molecules. Landfill leachate for example showed a more hydrophilic character as evaluated from the specific ultraviolet absorbance (SUVA) giving results below 2 L mg^{-1} m^{-1} [9], while others found that the dissolved organic carbon fraction in the MBR permeate was mostly neutral hydrophilic or hydrophobic, but also alkaline hydrophilic fractions were found [26]. This suggest the association (e.g. adsorption) of multiple components in the water.

Also physical properties like pH or temperature influence the properties of components (e.g. charge, dissolution ability) present in the water and therefore their mutual interactions. Two specific characteristics of the feed water matrix (related to wastewater treatment) are discussed more extensively below: the presence of natural organic matter (NOM) and in more detail the consequences of the interaction between NOM and cations for the filtration. Subsequently the effect of molecular weight distribution and seasonal changes is shortly addressed.

2.3.4.1 Natural organic matter

The presence of natural organic matter (NOM) can influence the membrane rejection of several compounds. For example, NF rejection of the target compounds (e.g. micropollutants) increased in the presence of an organics (NOM) rich solution matrix, such as the MBR permeate [15, 20, 34-37]. Also, rejection of endocrine disrupting compounds (EDC) and pharmaceutically active compounds (PhAC) was increased by the MBR permeate matrix, especially in the presence of organic matter. Significantly higher NF removal efficiency of EDCs and PhACs was found when using MBR effluent as a matrix compared to the filtration with Milli-Q water or natural surface water as matrix [20]. Increased pharmaceutical rejection by NF from 60% to above 80% in the presence of an MBR permeate matrix was noted [34]. Also the NF retention of cyclophosphamide was increased up to 90% when an MBR effluent matrix was treated, due to the occurrence of NOM adsorption on the membrane surface leading to membrane fouling [36]. Nevertheless, as a consequence also decreased NF permeability was observed when filtrating MBR permeate compared to Milli-Q water. Possibly also surface properties of the (fouled) NF membrane occurred. It was specifically mentioned that the occurrence of pore restriction was assumed to have the greatest influence on the rejection compared to changes in hydrophobicity or charge of the membrane surface. Association of target compounds with high molecular weight compounds can not only increase the rejection of micropollutants in NF, but can even establish rejection of components by MF or UF membranes, despite their much lower molecular weight compared to the MWCO of the membrane. Due to their association with larger molecules, e.g. micropollutants are even rejected by open MBR membranes [22, 34, 35]. On the other hand, this is not always the case and when no mutual interactions between the feed components occur, the earlier discussed removal mechanisms remain dominant. For example, the removal of sodium diatrizoate by NF was found to be similar for an ultrapure water matrix and an MBR permeate matrix (97% and 96%, respectively), and steric hindrance of the single diatrizoate itself with a size of 600 Da was considered the main rejection mechanism [11].

2.3.4.2 Cations and natural organic matter

In an MBR NF system the presence of both organics as well as cations is highly likely, and the occurrence and strength of mutual interactions is mostly determined by their concentrations. Both organics and cations can have a significant impact on the performance of MBR as well as NF membranes. MBR fouling can increase in the presence of cations such as calcium and magnesium and also the ratio between calcium and magnesium is important. Increased calcium concentrations (in comparison to the magnesium concentration) can decrease MBR membrane fouling as calcium is more effective than magnesium in binding and bridging the negatively charged functional groups that are present in EPS [38].

Also NF performance can be influenced by the presence of cations and organics. NF scaling in the form of calcium carbonate or calcium phosphate crystals can be inhibited by NOM/humic acids, which can for instance hinder the crystallization process [39]. Additionally, binding of cations to humics can also reduce the effective cation concentration and with that the availability of these cations for scale formation. Cations present in the feed solution of an NF membrane can interact especially with negatively charged target components or negatively charged natural organic matter (NOM). Cations therefore can not only cause changes in properties of the NF feed water matrix, but can also change the properties of a single target component in solution. For instance, it was found that increasing cation concentrations in the MBR permeate decreased the rejection of pharmaceuticals by the subsequent NF, due to lowering of the electrostatic repulsion forces between the negatively charged NF membrane and the target compounds (endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs) [37, 40]. At increased cation concentrations, the cations may even result in a reduction of the association of EDCs and PhACs with NOM (cations replace EDCs and PhACs in the NOM complex) [37], leading to significantly reduced rejection of EDCs and PhACs [20, 37]. Increased cation and NOM concentrations are also expected in an MBR NF process with NF concentrate recirculation as both cations and NOM are rejected by the NF and remain in the system.

2.3.4.3 Molecular weight distributions

Natural wastewater contains a multitude of components with a wide variety of molecular weights leading to a very broad molecular weight distribution. A general trend was found in MBR NF processes regarding the molecular weight distributions. The concentration of the larger organics fraction was reduced in the MBR, which led to an increase in the smaller organics fraction after the MBR compared to the feed. This fraction is then entering the subsequent NF process and may be a reason for increased NF fouling.

For example, when an organic fraction with molecular weight > 5,000 Da present in landfill leachate was fed to an MBR, the molecular weight of this fraction decreased due to the degradation of the substrate in the MBR (i.e. biotransformation) [9], or long aeration times or autolysis [26]. As a consequence, the MBR permeate showed a significant increase (44-60%) in the smaller soluble fraction (< 500 Da). Analysis confirmed a higher solubilization of the substrate and increased concentrations of soluble microbial products (SMPs) [9]. As this soluble fraction (in the MBR permeate) proceeds to the NF, it can cause organic fouling on the NF [9].

Other researchers confirmed this trend, and showed that the high molecular weight fraction of the inflow (MW > 10,000 Da) was completely broken down to lower molecular weight fractions by the MBR (mainly MW 5,000-10,000 Da but also MW < 1,000 Da). Breakup was related to aeration and bacterial autolysis [26]. This was also reported by Chon *et al*. [41] who found that after the MBR the organics fraction in the range of 820-900 Da increased, representing aromatic and protein-like substances. Correspondingly, increased polysaccharides concentrations from 6.7 mg L^{-1} in the feed to 8.9 mg L^{-1} were found in the MBR permeate. As already mentioned before, biological degradation of for instance molecules like lignin was assumed to be responsible for the increased concentration of the lower molecular weight fractions in the MBR permeate [41].

The above demonstrates that especially the degradation of higher molecular weight fractions in the MBR is an important aspect of MBR operation, as it causes and increase in the lower molecular weight organic carbon fractions in the MBR permeate (i.e. NF feed), which can affect the NF operation as well, as these small organics are known to be related to NF fouling [26, 41]. As the NF membrane retains the small organic compounds, in an MBR NF system with NF concentrate recirculation, these compounds will be redirected back to the MBR again, where they could also affect the MBR operation. Literature suggests that the increased retention times in the MBR in a system with concentrate recirculation can improve the biodegradation of those organics fractions [2]. However, in case the smaller organics remain an issue and cannot be further degraded in the MBR, additional treatments such as oxidation or adsorption can be considered as discussed later.

2.3.4.4 Seasonal changes

As compound rejection in both MBR and NF is dependent on the composition of the natural waters, rejection behavior may vary with seasonal changes, as also the composition of natural waters varies with the season [11]. It was found that for instance carbamazepine rejections using natural wastewater in the winter ranged from only 50-54%, whereas in the summer rejections up to 92% were measured, compared to a value of 74% when ultra pure water was used. Seasonal changes do have an impact on the rejection, but variations and effects are compound specific.

2.3.5 The fouling layer

Fouling and scaling on both the MBR and NF membrane are major aspects that deteriorate the membrane performance. Cake and gel-layer fouling are very common in wastewater applications. Cake layer formation in the MBR stems from the accumulation of solids (sludge) on the membrane surface, whereas gel-layer formation is often related to concentration polarization of macromolecules, e.g. extracellular polymeric substances (EPS) [42]. Gel as well as cake fouling require increased transmembrane pressures to maintain the flux, but can also decrease or increase rejection of compounds, especially in the MBR. Both gel and cake layers can cause a reduction in the actual pore size [43] of MF or UF membranes or provide additional adsorption sites.

In the case of NF, the use of real MBR permeate causes a fouling layer build-up in the form of a rough, dense and thick fouling layer on the NF membrane [20], containing mainly carbohydrates and proteins [34]. Also NF scaling can occur due to concentration polarization. Any type of fouling layer may change the membrane surface characteristics, such as surface charge or hydrophobicity, and consequently change the membrane performance (rejection and flux) [34, 35]. The fouling layer itself can also contribute to the rejection as it may show enhanced adsorption of specific compounds. A reduction in MWCO of the NF membrane by NOM adsorption (even smaller than e.g. micropollutants) was assumed to cause increased rejection [35].

2.4 Performance of MBR NF

2.4.1 Introduction

In literature, the performance of an MBR NF concept is usually evaluated in terms of conventional removal parameters (COD, N, P) i.e. the difference in concentration of certain species between inflow (feed) and outflow (permeate) and expressed as removal percentage. This holds for the MBR only, the NF only or for the entire MBR NF process from wastewater inflow to NF permeate. COD or TOC removal, nitrification (ammonium removal) as well as total nitrogen removal (nitrification + denitrification) are frequently reported. More detailed investigations also show inorganics removal and conductivity decrease as well as removal of specific industrial components such as color. A majority of the MBR NF literature though focuses on micropollutant removal. Therefore, especially the removal by NF of these small molecules, often present at low concentrations is discussed separately.

2.4.2 COD and TOC removal

Even though literature reports the treatment of different types of wastewater with MBR NF (landfill leachate, municipal wastewater, industrial wastewater (textile, food and beverage)), comparison of the results showed that COD removal percentages found in literature were comparably high in most MBR NF systems. Total COD removal in the MBRs ranged between 75-98% [6, 9, 13, 27, 44-48]. COD removal by the subsequent NF showed more variation ranging between 41-80% [9, 44, 49]. These variations in NF removal efficacy, especially in terms of the lower COD removal, were explained by the presence of high amounts of COD with a molecular weight below 500 Da in the MBR permeate (NF feed) resulting in low a degree of removal of this low molecular weight fraction by NF [9]. Literature also reported the use of an MBR NF process in the oil and gas industry [30]. Even though an extensive list of compounds present in the feed solution (produced water from oil/gas production) was given, primarily only COD decrease, conductivity decrease, hydrocarbon and oil/grease removal percentages were evaluated in this research. Also here, COD removal by the MBR only was in the expected range (83%). Hydrocarbon and oil/grease removal was > 99% and 70%, respectively [30]. Despite the challenging components present in the feedwater (e.g. heavy metals and phenols), the full MBR NF system still reached a COD removal of about 93-95% [9, 30].

In contrast, a COD removal of only 23% was found in an MBR treating landfill leachate [50]. This was explained by the low biodegradability of the treated water. Still, the full MBR NF system was very effective as more than 90% of the COD and TOC were removed, mostly due to the high removal efficiencies of the subsequent NF. This indicates that the combination of an MBR and NF is beneficial for feed waters with a lower biodegradability, as an appropriate NF membrane can contribute significantly to the overall removal of even smaller organics that cannot effectively be treated by the MBR only. This is confirmed by [6, 27, 44-47], who showed that nanofiltration as post-treatment was able to lower the COD (which is considered to be non-biodegradable) from an MBR permeate from 568-850 mg L^{-1} to a range of 23-120 mg L^{-1} or lower in the NF permeate. Additionally, in the case of alpha-keto gluconic acid removal (from landfill leachate), NF alone already showed removal results comparable to those obtained with a full MBR NF process. This makes the application of an MBR obsolete in this case [50]. Also in this case, the low removal by the MBR was the consequence of the low biodegradability of the components in the feed. TOC removal by the NF was usually in the range between 35 to 80% [9, 49, 51] and showed similar trends as COD removal. The combination of MBR NF showed an overall TOC removal of 96% [9, 13]. TOC concentrations in the NF permeate, when indicated, were usually less than 2-4 mg L^{-1} TOC [13, 27, 45-47].

Overall, literature shows that COD (and TOC) removal is generally high when the full MBR NF process is considered. Although MBRs are very well able to remove easily degradable components, additional NF as tertiary treatment is often critical to obtain the required permeate quality for water reuse. The reason for this is that the biodegradability of the compounds present in especially industrial wastewaters can vary significantly and often also low biodegradable compounds are present in large quantities in the waters to be treated, that cannot be removed by MBR only.

2.4.3 Nitrification, total nitrogen and total phosphorous removal

Biological nitrogen removal from wastewater typically occurs through aerobic nitrification (from ammonia to nitrate) and anoxic denitrification (nitrate to nitrogen gas). Generally, MBR NF literature presents rather high nitrification results. Full nitrification was even found when treating highly polluted landfill leachates [6, 29]. Also high nitrification of 88-95% for the treatment of textile wastewater or leachates was reported [9, 49]. However, as ammonium and nitrate are monovalent ions, their removal is mostly attributed to the MBR, rather than to the NF [9]. This implies that for total nitrogen removal especially the MBR operation and more specifically denitrification is essential.

In an MBR NF process, nitrate removal of 91%, down to at least 12.1 mg L^{-1} in the NF permeate was reached [13]. Others found total nitrogen removal of about 80% [13], as well as Total Kjeldahl Nitrogen (TKN) (organic nitrogen and ammonia) after the MBR of 82%, respectively. On the contrary, lower total nitrogen removal of only 20-25% was also reported, which was due to large variations in the concentration of N-containing species in the wastewater [49], which shows the dependence of the MBR performance in terms of nitrification on the wastewater composition. Overall, nitrogen removal varied substantially, which might be explained by the high variation in biodegradabilities of the COD in the wastewater needed for denitrification.

Total phosphorous could be satisfactory removed by the MBR NF concept: Biological removal of total phosphorous in the MBR alone of more than 50%, and 99% by the full MBR NF system was obtained, resulting in an NF permeate containing 0.06 mg L^{-1} total phosphorous only [13].

2.4.4 Inorganics and conductivity

In general the MBR operation has hardly any contribution to salt removal, and the subsequent NF is responsible for the conductivity decrease [6, 30, 44, 48]. Only a slight decrease in salt content of only 7% could be attributed to biological activity [13]. Final NF permeate concentrations between 0.175 mS cm^{-1} are reported [27, 45-48], although also values as high as 6.077 mS cm^{-1} conductivity and 4,077 mg L^{-1} TDS (total dissolved solids) are presented [44]. Of course, the actual salt concentrations in the NF permeate depend on the conductivity of the inflow (wastewater feed subsequent MBR permeate) but especially also on the type of NF membrane selected. As such, the observed conductivity decrease obtained by the NF ranged between 20-40% [30], but also values < 35% [6] or as high as 60-73% were reported [48, 49].

2.4.5 Color removal

The NF membrane is not only responsible for salt removal but contributes to the removal of remaining organic matter from the MBR permeate [49] and colorants, which is especially relevant for the textile industry. The color removal efficiency of the NF is determined by the type of color, but especially by the biodegradability of the specific colorants.

De Jager *et al.* reported that color removal of azo dyes by an MBR was only 28.6%, and therefore the application of NF as post-treatment was critical to treat low biodegradable substances present in the wastewater and consequently in the MBR permeate. The NF resulted in additional color removal of 97.6%, and the entire MBR NF setup therefore could achieve high color removal of 98.3% [44].

Removal of azo dyes from textile wastewater can also be improved with and additional anaerobic stage as azo dyes are known to be degraded under anaerobic conditions [49]. An anaerobic biofilter in front of the MBR increased the color removal up to more than 95% and a COD concentration in the MBR permeate below 96 mg L^{-1}. The subsequent NF removed another 70-90% of the remaining color [49], although this could also be related to the slightly lower COD inflow values of < 1,200 mg L^{-1}.

A rather exceptional batch-culture application of MBR NF reported in literature is the treatment of special reactive dye containing wastewaters from the textile industry. Results showed that the use a white-rot fungi culture in the MBR reactor specifically increased the color removal efficacy. Depending on the specific color compound, the fungi MBR NF combination achieved color removal efficiencies up to 99%, which makes this process a very sustainable alternative to conventional processes such as adsorption, UV or H_2O_2 treatment [51]. As such, depending on the application and components in specific wastewaters, also other additional tailored treatments to remove specific components that cannot be removed by the MBR NF process may be required to produce reusable water.

2.4.6 Treatment of micropollutants

2.4.6.1 Introduction

Dedicated treatment of micropollutants is of special importance as these components are of great concern in terms of environmental considerations and health. Especially when the product water is intended for reuse, the presence and concentration of micropollutants is critical. Micropollutants are organic or mineral compounds that end up in wastewater at concentrations in the range of µg L^{-1} to ng L^{-1}. They can be environmentally harmful, have serious health risks, are highly water soluble and persistent against conventional treatment processes [8]. Micropollutants are small molecules such as pesticides, pharmaceuticals or endocrine disrupting compounds. Maximum allowable concentrations of some micropollutants are regulated in the directive 2008/105/EC [52] for priority compounds in surface water. However pharmaceuticals and hormones are not yet included in the directive.

The main focus of MBR NF literature is on the removal of these micropollutants, because of the high removal capacity of micropollutants by NF, combined with a preceding biological stage in the MBR. The emerging number of papers dealing with MBR NF for micropollutants removal is directed by the increasing water demand and increasing concern regarding these substances (but also because of the lower detection limits of the current analytical equipment). Necessary upgrades of conventional wastewater treatment plants for micropollutant removal are not unlikely in the future in order to accommodate the regulations.

2.4.6.2 Performance of MBR and NF

Even though MBRs were found to be sufficient for removal of most hormones and a majority of pharmaceuticals [51], improved removal of especially polar and non-biodegradable compounds requires a tertiary treatment step such as NF. In general low removal capacities of micropollutants (mostly below 50%) by an MBR only were found for a multitude of components, due to their hydrophilic, non-biodegradable character: acetaminophen, atenolol, atrazine, carbamazepine ciprofloxacin, DEET, diclofenac dilantin erythromycin, fenoprop, glimepiridine, ibuprofene, iopromide, linuron, meprobamate, naproxen, pentachlorophenol, primidone, propyphenazone, TCEP, triamterene, and trimethoprim [13, 15-17, 19, 50, 53, 54]. Nevertheless, an MBR serves as an excellent pretreatment for the NF, and a combined MBR NF process has a high capacity to remove micropollutants.

The majority of the removal of micropollutants is in many cases specifically attributed to the NF membrane. For instance, 95% NF removal of macrolides, sulfonamides and fluoroquinolones, and 85-95% removal for trimethoprim was reached by the NF treating synthetic wastewater that was prior fed to an MBR [19]. Even when real hospital wastewater was treated with MBR NF, the NF removed an additional 80-99% of all 11 tested compounds (bezafibrate, bisoprolol, carbamazepine, clarithromycin, ciprofloxacin, diclofenac, ibuprofen, metronidazole, moxifloxacin, telmisartan and tramadol) [18]. The MBR itself was not able to remove those compounds sufficiently. Similar results were found for 4-octylphenol, bisphenol A, estrone, 17 ß-estradiol, 17 α-ethynyl estradiol and genistein [55], where the combination of MBR NF assures low release of estrogenic active compounds with the final permeate. Estrogenic activity was effectively reduced from 0.65 ng-EEQ L^{-1} in the MBR permeate (NF feed) down to 0.23 ng-EEQ L^{-1} in the NF permeate (EEQ: total estrogenic activity measured as the 17β-E2 equivalent quantity) [55]. Nevertheless, not for all compounds high NF removal percentages were found. Removal percentages of 4-octylphenol, acetaminophen, carbamazepine, and dilantin for example remained below 70% [13]. This was confirmed by other researchers, who showed that not all compounds can be addressed similarly well. In some cases therefore additional RO stages were even considered [18].

Unfortunately, not all MBR NF literature actually mentions the specific removal capacity of the MBR separately. Most researchers use existing MBR permeate as a matrix for NF filtration test, without investigating the combined MBR NF process. However, the contribution of the MBR in terms of removal efficacy should not be ruled out, as only the full MBR NF process has the potential to remove up to 95% of most compounds (and not only micropollutants are of importance) [13, 54].

2.4.6.3 Nonylphenol and bisphenol A

Some literature specifically focuses on the removal of phenolic EDCs (endocrine disrupting compounds) such as nonylphenol (NP) and bisphenol A (BPA). Such EDCs result from various sources, but mainly from the plastics industry, and are likely to end up in the wastewater. The removal of NP by an MBR is generally reported to be around 85%, though it is not always clear whether this is due to biodegradation, adsorption or air stripping [29, 56]. Contradictory, also lower removal percentages for NP by the MBR (55%) have been found [55], which underlines the consideration that the removal mechanism is probably not only related to microbial degradation in the MBR, as that would generate rather reproducible results. Laboratory NF experiments showed that NP rejection by NF was above 70% for all 11 tested NF membranes [29].

BPA removal by an MBR was even higher (above 90%) [55] and the NF rejection of BPA for 11 different NF membrane varied between 65% up to nearly 100% [29]. This was supported by the work of Wintgens *et al.*, who pointed out that e.g. BPA removal is attributed to biological degradation, and as such benefits from long SRTs, as well as to the association of BPA with macromolecules in the MBR supernatant. NP removal on the other hand is to a great extent attributed to NF rejection rather than to biological degradation [22]. Overall, removal of NP by the full MBR NF process was slightly lower (80%) than that of BPA (95%) [55, 56], which indicates that biological degradation contributes significantly to the overall removal as in the case of BPA.

2.5 Membrane foulants and cleaning strategies

2.5.1 Introduction

Despite the type of membranes used and the specific wastewater selected, fouling and scaling of both the MBR and the NF membranes will occur and decrease the performance of the process considerably. A good performing MBR serves as a pretreatment step for the tertiary NF, and a good performing NF results in the production of large amounts of high quality reusable water. Consequently membrane cleaning is very important in a combined membrane application like MBR NF to ensure the production of high quality reusable water. Both physical and chemical cleanings of the MBR and nanofiltration membranes are applied. Especially chemical cleaning of the MBR not only affects the MBR membrane operation, but also the subsequent NF step components used for the chemical cleaning of the MBR can end up in the NF feed (MBR permeate) [47]. This becomes even more important when NF concentrate recirculation to the MBR is applied. In that case, also the cleaning of the NF membrane can affect the preceding MBR, as due to concentrate recirculation, components used for cleaning of the NF membrane either end up in the product water or are recirculated back to the MBR and can accumulate in the system. Consequently, appropriate cleaning strategies are necessary for combined MBR NF systems in order to assure continuous, high quality operation. Several cleaning strategies are applied in MBR NF systems, which are summarized below.

2.5.2 MBR

Regular membrane cleaning in the MBR assures a proper process performance. MBR membranes can be impacted by both hydrophilic and hydrophobic fractions of organic matter in the mixed liquor [41]. It was found that mainly hydrophobic compounds like humics adsorb on the MBR membranes which, can diminish MBR performance.

2.5.2.1 Physical cleaning and backwashing of the MBR

Especially in industrial applications, where bacterial stress can occur due to for instance industrial chemicals, the filterability and dewaterability of MBR sludge can be influenced by high EPS contents [45]. Depending on the membrane modules, backwashing of the MBR membrane can be used to restore the flux of the MBR and consequently of the subsequent NF. This was done in an MBR NF process treating spent water from a fruit juice process [47]. It was suggested that the water necessary for the backwash process could be reused water from the system [27, 47]. The use of NF concentrate for backwashing of the MF membranes was possible when its TOC value was below 200 mg L^{-1} [47]. Nevertheless, it was found that additional chemical cleaning was still necessary and more favorable for disinfection and prevention of fouling [47].

2.5.2.2 Chemical cleaning of the MBR

MBR membranes can be chemically cleaned externally (ex-situ) or in-situ (cleaning in place – CIP), depending on the configuration. Several chemical cleaning agents are suggested for MBR NF processes. In the mentioned fruit juice process, oxidizing agents were most successful for CIP [47]. Cleaning was performed with 0.2-0.5 g L^{-1} NaOCl, which restored the permeate flux from 10-20 LMH up to 28 LMH [27]. However, after upscaling of this system, this strategy had to be changed to H_2O_2, due to formation of disinfection byproducts in the form of adsorbable organically bound halogens (AOX) [46]. This shows that especially when the water is reused (as is the case of NF concentrate recirculation), production of disinfection byproducts is an important issue and has to be prevented. An additional treatment such as ozonation can be applied afterwards to remove the byproducts as will be discussed later, however, this requires an additional (cleaning) treatment. In the same work trials with ex-situ cleaning were performed and considered to be effective but expensive. In order to not affect the NF membrane material by the cleaning agent used for the MBR, simultaneous cleaning of both membrane systems was suggested [47]. Besides the use of NaOCl to remove organic contamination, citric acid was suggested for removal of inorganic scaling [44]. MBR cleaning was mainly based on NaOCl to remove organic fouling, although in some cases also acidic cleanings were applied to remove scaling.

2.5.3 NF membrane cleaning

The nanofiltration step applied after the MBR can be impacted by both organic or inorganic compounds causing NF flux decline. Calcium, silica, manganese and iron were reported as scaling contributors [57]. Also phosphorous and magnesium were mentioned to contribute to scaling [58]. Organic foulants such as hydrophilic organics (polysaccharides), i.e. non-humic substances [41], or amino acids [58] were mentioned in literature as foulants as well.

Acidic, basic as well as complexing agents can be used to restore the flux of an NF membrane. Homemade hollow fiber NF membranes were cleaned successfully after 6 days of permeation using 0.01 M HCl, which restored the permeate flux to 96% of its initial value at day 1 [6]. Others found HCl (pH 2) cleaning to be most effective to restore the NF flux. Application of a final alkaline cleaning step after acidic cleaning did not show any additional contribution to the flux recovery. This suggests that the NF membrane fouling was dominated by the contribution of inorganic constituents and mostly silica scaling occurred, which was confirmed by ICP analysis [57]. In contrast, others found organic fouling to be the main cause for flux decline of the NF membrane and a 0.1% NaOH solution was most effective for NF cleaning. Alkaline cleaning however reduced the surface hydrophobicity of the membrane surface [58] and not all organic fouling could be removed by the NaOH treatment. To improve the cleaning efficiency, an additional cleaning step using (citric) acid cleaning was added prior to the NaOH treatment to remove inorganic salts. Flux data were provided for different series of multiple cleaning steps, and it was mentioned that more brown color remained on the membrane surface when alkaline cleaning was followed by acidic cleaning. Lowest membrane surface roughness was obtained with citric acid cleaning. Finally, a combination of alkaline and acidic cleaning and an additional chemical disinfection step (0.1% peracetic acids) applied 1-2 times per week was suggested to be effective in terms of final product quality and production rate [27].

The main results regarding membrane cleaning in an MBR NF process presented in literature and shortly summarized above shows that membrane fouling and the subsequent cleaning strategies on both the MBR membrane as well as on the NF membrane show a broad variation and strongly depend on among others the type of feed water used, but also the specific membrane properties. Not only the type of cleaning is relevant in this aspect, also the order of the different cleaning steps can make a significant difference in terms of cleaning efficacy, depending on the type of fouling/scaling (i.e. organic or inorganic fouling) and depending on the significance of the two different organic or inorganic fouling types.

2.6 NF concentrate recirculation

2.6.1 Introduction

One of the major drawbacks of wastewater treatment in in many wastewater treatment processes, and also in an MBR NF concept, is the production of a concentrated waste stream. A sustainable approach suggested to reduce the amount of waste, is the recirculation of the NF concentrate back to the sludge treatment facilities of a treatment plant, as otherwise disposal elsewhere is required [29]. Additionally, also the use of NF concentrate as MBR backwash fluid was suggested (when the TOC is below 200 mg L^{-1}) [47].

When MBR NF processes are considered, the concentrate exiting the NF unit is a major waste stream. A sustainable approach to reduce the production of such highly concentrated streams in an MBR NF concept, is the option of an MBR NF process with integrated concentrate recirculation [2, 47, 50], as further discussed and investigated in this thesis. Concentrated waste streams can also be considered as an important source for the recovery of valuable components, especially as the waste stream is highly concentrated, which facilitates the recovery compared e.g. highly diluted streams. The proposed approach of and MBR NF with concentrate recirculation has this additional benefit that it allows the simultaneous recovery of valuable components. The most important literature on NF concentrate recirculation is summarized below.

In 1994 the first MBR NF combination, patented by Wehrle Umwelt GmbH [1], was presented as BioMembrat-Plus® [2]. It was stated that the process was applicable even for the treatment of highly polluted landfill leachates (COD: 1,000-4,000 mg L^{-1}). An additional oxidation step with ozone or an activated carbon adsorption stage was added to the concentrate recirculation loop to lower the accumulation of non-biodegradable organics [59]. The treated NF concentrate was subsequently recirculated back to the MBR. The MBR in the BioMembrat-Plus® process was able to remove 74% of the inflow COD, the COD removal by the full MBR NF process was as high as 99%. Nevertheless, the at that time proposed MBR NF process exceeds the current discharge limits for COD of 200 mg L^{-1} (due to concentrate recirculation) and as such requires a bleed stream [2]. In 1997, the incorporation of a so-called ECOCLEAR® process (a heterogeneous catalytic ozonation stage) into the concentrate loop of the BioMembrat-Plus® MBR NF process to treat landfill leachate was presented. With this process COD concentrations in the NF concentrate could even be reduced from 5,000 down to 500 mg L^{-1} [60]. Again the ECOCLEAR® process lowered the impact of the NF concentrate recirculation and improved the NF permeate quality. A COD concentration of only 60 mg L^{-1} in the NF permeate was obtained, which was below the target limit of 200 mg L^{-1}.

Ten years later Robinson reported a larger scale (60 m^3 day^{-1}) MBR NF (BioMembrat-Plus®) installation. The process was able to treat even higher COD loads of 5,000 mg L^{-1} and reduced the COD in the NF permeate down to < 100 mg L^{-1} (> 98% removal) [61], meanwhile mentioning that the NF concentrate could be recirculated back to the landfill site. Unfortunately no further information on process design or development was given.

Despite these first early developments of the MBR NF recirculation concept, it remains still questionable whether additional concentrate treatment as carried out in the BioMembrat-Plus® process is actually necessary, as will be discussed below, especially when municipal wastewater is used instead of highly polluted leachates.

2.6.2 Challenges of concentrate recirculation

2.6.2.1 Biological degradation

NF concentrate recirculation in an MBR NF process prolongs the retention time of compounds that are not or hardly biodegradable (and that are rejected by the NF). A high NF retention of slowly biodegradable compounds can increase the biodegradation [22, 46] especially when combined with a low retention of inorganic salts to avoid high conductivities [46, 62]. In literature, MBR NF processes with full concentrate recirculation [2, 47, 63], but also an example with partial RO concentrate recirculation showed enhanced biodegradation [5]. From the available literature it is however not clear whether the growth yield of the bacterial community really increased or that only the COD removal was increased, nor which mechanisms were responsible for this. A more detailed study including a full COD mass balance would be needed to investigate the MBR process in more detail.

2.6.2.2 Nitrification and denitrification

Concentrate recirculation can have a detrimental effect on the nitrogen removal in case toxic compounds are recirculated back to the MBR. NF concentrate can increase concentrations of toxic compounds, e.g. heavy metals, which can decrease the activity of the nitrifiers in the sludge and consequently diminish the nitrification performance of the wastewater treatment plant. The first MBR NF plant with concentrate recirculation (BioMembrat-Plus®) treating landfill leachate, reached NH_4-N removal percentages of 99% down to values of 10 mg L^{-1} in the NF permeate [2]. Direct NF concentrate treatment with the additional ECOCLEAR® process further improved the NF permeate quality resulting in NF permeate concentrations of NH_4-N and N-total of 0.2 and 50 mg L^{-1}, respectively [60]. Also in a larger, 60 m^3 a day, MBR NF plant, nitrifiers could decrease the NH_4-N concentration in the NF permeate down to < 1 mg L^{-1}, despite the high wastewater feed load of 2,000 mg N L^{-1} [61]. Nitrification and denitrification performance was not affected by the NF concentrate recirculation. Unfortunately no further systematic evaluation of the potentially hazardous behavior of for instance heavy metals in combination with concentrate recirculation was performed to evaluate the performance on the longer term.

2.6.2.3 Conductivity

The conductivity is a very important parameter as increased conductivity in the MBR reactor can deteriorate the MBR process due to osmotic pressure effects that affect the bacteria or sludge deflocculation. When NF concentrate recirculation is considered and especially when NF membranes with high retention for salts are used, as enrichment in salts in the MBR reactor can occur. Industrial MBR NF processes without concentrate recirculation show that conductivity of the NF concentrate can be as high as 15 mS cm^{-1} (3.5 g L^{-1} sodium) [46]. Recirculation of this high salt loaded stream back to the MBR would be harmful for the MBR performance. The choice of NF membrane thus is critical. So far however, no systematic research on this topic exists.

Also in terms of the NF operation, conductivity plays an important role. NF concentrate recirculation to the MBR can decrease the NF rejection for chloride and nitrate, but also that of other ions [2]. Higher feed loads decrease the effectiveness of Donnan exclusion of the NF membrane. During treatment of landfill leachates with MBR NF [2], chloride and nitrate rejections of the NF of 11 and 13% were found, whereas for sulphate (bivalent ion) a value of 96.5% was obtained. The corresponding concentrations in the NF permeate were < 2,500 mg L^{-1}, < 750 mg L^{-1} and 53 mg L^{-1}, respectively. High chloride concentrations (1,200 mg L^{-1}) were also obtained in the NF permeate of a large scale MBR NF process [61]. The corresponding conductivity was 10 mS cm^{-1} [61]. Despite this, in a conventional MBR NF application based on municipal wastewater, it is not that likely that the conductivity will significantly deteriorate the NF operation, but more research regarding this aspect is needed.

2.6.2.4 Membrane fouling

Concentrate recirculation can also result in increased fouling and especially scaling of both the MBR and NF membranes. The occurrence of fouling in the case of full concentrate recirculation is hardly reported in literature. Jacob *et al.* (2010) for instance pointed out that an overall slightly higher concentrated MBR permeate (mostly organics and salts (increased conductivity)) showed much higher flux decline of the NF compared to MBR permeate with lower concentrations at the same feed pressure (8 bar) [6]. However, for a more profound discussion on this topic, more research regarding MBR and NF membrane performance with full concentrate recirculation without any further treatment is required.

2.6.3 Additional treatment in an MBR NF process with concentrate recirculation

When nanofiltration concentrate recirculation is applied, some components (mainly dissolved organics) can accumulate in the system and may need additional treatment in either MBR or NF permeate to meet the discharge limits. Several intermediate treatment options are suggested to improve the product quality obtained in an MBR NF recirculation process: 1. Improvement of biodegradation; 2. Additional removal to meet regulated discharge limits; 3. Improvement of membrane filtration. Though, the three categories cannot be considered independent of each other.

Already in the first MBR NF process mentioned in 1994, additional treatment of the recirculated concentrate stream was applied to improve the degradation of hardly biodegradable organic compounds [2]. UV, ozone (0.13 - 0.18 kgO_3 m^{-3}) and activated carbon were suggested to be included in the concentrate loop. Later, the ECOCLEAR® process was suggested as a catalytic oxidation stage (0.8 $kgO_3/kg_{\Delta COD}$) for additional treatment of hard-to-degrade components. This process improved the quality of the NF permeate and was able to meet the discharge requirements. In addition, the ECOCLEAR® process also decreased AOX (adsorbable organically bound halogens) concentrations in the NF concentrate from 4.8 mg L^{-1} down to 1 mg L^{-1} [60].

In terms of micropollutants, the application of an advanced oxidation process to treat the NF concentrate in an MBR NF process with NF concentrate recirculation did not contribute to a large extent to the elimination of nonylphenol (1.6%), as biodegradation is the dominant mechanism for nonylphenol removal [56]. The article does not mention any changes in the biodegradability of nonylphenol due to the addition of the oxidation step.

However, as literature on the effect of NF concentrate recirculation on the removal of specific micropollutants or the necessity to include additional treatments to remove micropollutants is still limited, more research is required to address this issue. It was for instance reported that an additional 50% removal after the MBR can be reached when an additional granulated activated carbon (GAC) stage after the MBR is added [29]. Bisphenol A (BPA) removal in an MBR followed by a powdered activated carbon (PAC) stage [56] even reached a removal percentage up to 97.8%. On the other hand, a high BPA removal percentage of 95% by the MBR only (without any additional treatment) was also found [56]. Potential dangers and improvements in terms of biodegradability and MBR NF operation due to the addition of extra treatment processes should be addressed well, especially when also concentrate recirculation is applied. Finally, also the consequences of additional treatment on membrane fouling need to be considered as for instance NF permeability increased after treatment of MBR permeate (NF feed) with ozone [53].

2.7 Conclusions and future research

Water scarcity and more stringent regulations force the industry in the direction of wastewater purification and water reuse. This chapter summarized the literature on MBR NF processes and reflected on the potential opportunities and challenges.

A combined MBR NF process is potentially very attractive for wastewater treatment, as it combines a microbiological treatment and a separation step. This enhances increased removals of a multitude of components present in wastewater. The tertiary NF treatment used to polish the MBR permeate guarantees the production of high quality, reusable product water

(NF permeate). Recirculation of the concentrate back to the MBR reduces the waste stream and results in higher removal percentages as due to the increased retention time because of concentrate recirculation, especially components that are difficult to remove, show increased biodegradation. Combined with the NF operation, high quality, reusable water is produced as the NF permeate.

Only a limited number of MBR and NF processes with partial or complete concentrate recycle were described in literature. To assess the real potential and the remaining challenges of such an integrated MBR NF process with concentrate recirculation, requires more detailed, systematic research regarding MBR and NF performance in terms of e.g. microbiological activity, MBR and NF membrane performance, fouling and scaling, and the possibility to recover valuable components (e.g. phosphorous) from the process.

List of Abbreviations

AOX	Adsorbable organically bound halogens
BOD_5	Biochemical oxygen demand (measured over 5 days)
CAS	Conventional activated sludge
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
EDC	Endocrine disrupting compounds
EPS	Extracellular polymeric substances
GAC	Granular activated carbon
HRT	Hydraulic retention time
MBR	Membrane bioreactor
MF	Microfiltration
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PhACs	Pharmaceutically active compounds
RO	Reverse osmosis
SMPs	Soluble microbial products
SRT	Solids retention time
SUVA	Specific ultraviolet absorbance
TDS	Total dissolved solids
TOC	Total organic carbon
TSS	Total suspended solids
TKN	Total Kjeldahl Nitrogen
UF	Ultrafiltration

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3

Impacts of NF concentrate recirculation on membrane performance in an integrated MBR and NF membrane process for wastewater treatment

This chapter will be submitted:

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Abstract

Combining membrane bioreactors with nanofiltration (MBR NF) offers a way to produce reusable water from municipal wastewater. The environmental problem of NF concentrate waste streams can possibly be resolved by recirculation of the NF concentrate to the MBR. In this study this MBR NF recirculation concept was tested, and the results were compared to a reference MBR without concentrate recirculation. The biological performance of the MBR in terms of COD removal and nitrification was not affected by concentrate recirculation. The sludge production was reduced by 21%. The sludge flocs improved in quality. They were more compact, exhibited better settleability and were less prone to shear, which are important factors in reducing sludge treatment costs. Fouling of the MBR membranes was more severe than in the reference system. This was mainly caused by recirculation of non-biodegradable (soluble) organic compounds. Hence, further membrane and other system improvements are needed to solve this fouling problem.

3.1 Introduction

After appropriate treatment, municipal wastewater can be reused as a secondary resource for reuse, for instance as industrial process water. In highly populated delta regions and other regions facing water scarcity, this can help to relieve the pressure on the available fresh water resources. In conventional municipal wastewater treatment plants equipped with secondary settlers, the effluent quality is highly variable and strongly depends on biological performance and solids settleability. The integration of a physical barrier, such as in a membrane bioreactor (MBR), guarantees high quality and solids free effluent, which subsequently can be upgraded to industrial process water by nanofiltration (NF) or reverse osmosis (RO) [1-4].

NF and RO systems produce large volumes of concentrate, typically 10-20% of the wastewater volume, and these concentrates may contain large amounts of mono- and multivalent ions, humic-like compounds, heavy metals and organic micropollutants such as pharmaceuticals and personal care products. Common, but non-sustainable disposal routes for NF and RO concentrates are discharge to surface waters, groundwater, sewers or landfills [5-7]. To make the production of reusable water more sustainable, the concentrates could be recirculated to the MBR system for further degradation of organics and uptake of inorganics by the (biological) sludge. Remaining pollutants are discharged with the excess sludge, which has a much smaller volume than the NF concentrate. For RO concentrates full recirculation is not an option because RO membranes have a much higher monovalent ion rejection than NF membranes and full concentrate recycling would dramatically increase the salinity in the MBR, resulting in poor biological performance [8]. In addition, performance of the MBR membranes can become much worse at higher salinity levels [9].

For MBR systems not equipped for biological or chemical phosphorus removal, high phosphate levels in the NF concentrate could accommodate economically feasible phosphorus recovery [10]. Additionally, NF concentrate recirculation could enhance MBR NF performance. Firstly, NF concentrate recirculation extends the (biological) contact time for organic micropollutants, which for some of these could result in enhanced biodegradation [2, 11,12]. Secondly, elevated concentrations of multivalent cations such as calcium, magnesium and iron in the NF concentrate could improve the bioflocculation process in the MBR because they form bridges between the negatively charged extracellular polymers (EPS) that are produced and excreted by the microorganisms [13]. A good bioflocculation process improves the filterability of the sludge and NF concentrate recirculation thus may help to reduce membrane fouling. However, it is recognized that NF concentrate recirculation also may have a negative impact on MBR performance. For example, NF rejection of heavy metals will raise their concentration in the MBR and this could inhibit nitrification and biological COD removal.

Knowledge about the biological performance of combined MBR NF or MBR RO systems with concentrate recycling is scarce. Krauth *et al.* [11] investigated an MBR NF system for textile and tannery wastewater treatment and reported an enhanced biodegradation in the MBR and a very low sludge production. Successful treatment of food industry wastewater by an MBR NF process was described [14]. They achieved a water recovery of 80% and a water quality meeting the standards for reuse. Tansel *et al.* (2005) presented results on (partial) recirculation of RO concentrate within an MBR RO process. The concentrate caused slightly increased sludge concentrations, but also higher total organic carbon (TOC) concentration in the MBR permeate. Joss *et al.* [2] investigated an MBR RO process with concentrate recirculation for municipal wastewater treatment. They focused their research on prevention of membrane scaling and on removal of pharmaceuticals. Detailed data on the biological performance of the MBR in relation to concentrate recirculation were not provided.

In this study a combined MBR NF system for municipal wastewater treatment with 100% NF concentrate recirculation to the MBR was investigated for a period of 220 days. The effects of full NF concentrate recycling on fouling of the MBR membranes and the NF membrane were reported earlier [15]. In this contribution the biological treatment performance in terms of COD removal and nitrification, including a COD mass balance as well as several sludge characteristics were compared to a reference MBR without NF concentrate recirculation. Based on the results of this comparison the feasibility of a combined MBR NF system for municipal wastewater with full concentrate recirculation will be discussed.

3.2. Materials and Methods

3.2.1 MBR and NF operation

Two identical 7 L MBR lab scale reactors, designed for COD removal and nitrification (Fig. 3.1), were operated for a period of 220 days. Both MBRs were operated at a solids retention time (SRT) of 16 days and were fed with pre-settled municipal wastewater, collected from the local sewer system. Each reactor was equipped with two submerged flat sheet microfiltration membrane plates (Kubota, Japan), with a nominal pore size of 0.4 µm. The average operational flux was 6.4-7.5 L m^{-2} h^{-1} (LMH) and the membrane area was 0.116 m^2 per plate. Aeration to provide oxygen for the microorganisms and for membrane scouring was combined and supplied by coarse bubble aeration plates. The MBR reactors always received identical air flow rates to ensure that membrane scouring was equal.

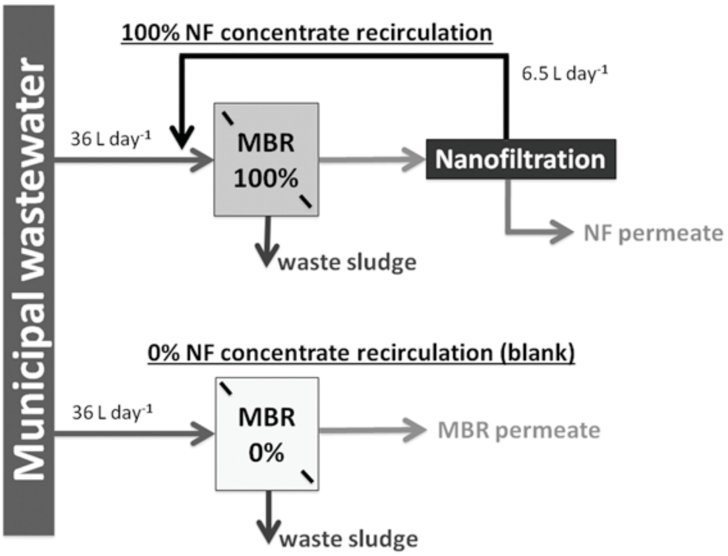


Fig. 3.1 *Process scheme of the MBR systems with full (R100%) and without (R0%) NF concentrate recirculation.*

One MBR system was operated without NF concentrate recycle (R0%) and the permeate from this MBR was discharged to the sewer without further treatment. The second MBR (R100%) received fresh wastewater and additionally to that the entire NF concentrate produced by the subsequent NF step. To establish this recirculation loop, the MBR permeate of R100% was collected in a 600 L storage tank for a period of two weeks. After two weeks this permeate was concentrated using an NF unit, equipped with a 2.5 inch spiral wound NF270 module with a surface area of 2.6 m^2 (DOW). This particular NF membrane was selected because of its low NaCl and high phosphate rejection [15]. NF rejections for relevant compounds (Table 3.1) were calculated from concentrations in the mixed permeate storage tank and three grab samples of NF permeate. Rejections of heavy metals other than copper could not be calculated because concentrations were below detection limits. A 98% rejection of ammonium ions was calculated but it is unlikely that this high rejection was caused by membrane rejection alone. Probably also precipitation of ammonium occurred.

Table 3.1 *Average NF rejection for various compounds during concentration of 8 batches of MBR permeate (every two weeks over a period of 120 days) [15]. The relatively high standard deviations were caused by variations in wastewater and NF feed composition.*

Compound	NH_4-N	NO_3-N	PO_4-P	Ca	Cu	Mg	Na	K	Cl	COD
Rejection (%)	98 *	6 ± 8	99 *	57 ± 12	79 ± 13	78 ± 11	31 ± 12	21 ± 18	36 ± 13	92 ± 7

*NF permeate < 0.1 mg L^{-1}

The NF was operated at a feed pressure of 11 bar and the average water recovery was set to 85%. The 100 L of NF concentrate that was produced in this manner was fed continuously to the R100% MBR. Both MBRs received 36 L day^{-1} of pre-settled wastewater, equivalent to a hydraulic retention time (HRT) of 4.7 h, whereas R100% received an additional 6.5 L day^{-1} of NF concentrate.

The temperature and pH in the two MBR systems were measured with a portable pH meter (WTW Multi 340i) and were 16.7 ± 2.1 ˚C and 7.5 ± 0.2, respectively over the whole experimental period. The dissolved oxygen concentration (DO) in the MBRs was measured with a portable DO sensor (Hach Lange HQ40d) and was manually controlled around 2-4 mg L^{-1} (same airflow in both systems). At equal air flow rates the DOs in R0% and R100% were 2.2 ± 2.5 and 3.2 ± 2.5 mg L^{-1}, respectively. The transmembrane pressure (TMP) of the MBR membranes was continuously monitored by pressure sensors (Endress + Hauser, Cerabar M). Whenever the TMP in one of the MBRs exceeded 400 mbar, the membranes were removed from both reactors for physical and chemical cleaning as described in more detail by [15]. Membrane fouling in R100% was more severe and the membrane fouling rate in this MBR therefore determined the cleaning frequency, which was once every two weeks.

3.2.2 Sampling and analytical methods

Grab samples from the wastewater, MBR sludges and MBR permeates were taken twice a week over a period of 220 days. All samples were immediately processed. On the wastewater and MBR sludge samples a sequential paper filtration (Whatman Black Ribbon 589/1, 12-25 μm) and 0.45 μm filtration (Cronus, PTFE) were performed. NF permeate samples were taken three times during the production of each batch of NF concentrate, which was performed every two weeks. Of the results, only the last 120 days were taken into account for further interpretation because after a startup phase during this period the reactors exhibited a stable process performance.

COD concentrations were determined according to standard methods [16] with different Hach Lange COD test kits, depending on the concentration. The difference between total COD and paper filtered COD will be referred to as suspended COD, the difference between paper filtrate and 0.45 μm filtrate as colloidal COD and the COD of the 0.45 μm filtrate as dissolved COD. Ammonium was determined in 0.45 μm filtered samples by LCK 303 and LCK 304 test kits (Hach Lange GmbH) and total nitrogen in unfiltered samples by LCK 338 (Hach Lange GmbH). BOD_5 of the wastewater was determined with LCK555 test kits (Hach Lange GmbH).

Concentrations of anions, elements and inorganic and organic carbon were determined in 0.45 μm filtered samples. Anions were analyzed by ion chromatography (Compact IC 761, Metrohm) and elements by inductively coupled plasma (Optima 5300 DV, Perkin Elmer). Total inorganic and total organic carbon were determined by a Shimadzu TOC-VCSH.

Total suspended solids (TSS), volatile suspended solids (VSS) and ash content in sludge samples were determined according to standard procedures [16]. In addition, sludge samples were centrifuged for 1 min at 3,500 rpm and 0.5 g of the pellets was digested (45 minutes at 180 °C) with nitric acid (65 wt%, VWR BDH Prolabo) in a microwave oven (Ethos One, Milestone). Element concentrations were subsequently analyzed with ICP-OES (Optima 5300 DV, Perkin Elmer). The same digestion procedure was used for the wastewater solids. For this, 0.3 mL nitric acid was added to 10 mL of wastewater.

Humic acid concentrations in 0.45 μm filtered samples were determined occasionally towards the end of the operational period by liquid chromatography organic carbon detection (LC-OCD, Model 8; OCD-detector: Siemens Ultramat 6^E; Column: Toyopearl HW-50S, 30 μm, 250 mm; UV-detector: Agilent 1260 Infinity; OND-detector: Agilent 1260 Infinity).

The sludge volume index (SVI) of MBR sludges was determined once a week according to standard procedures [16], except that a sludge volume of 100 mL was used. Light microscopy (Leica DMI 6000B, Leica) was frequently performed on sludge samples to inspect floc structure and presence of protozoa.

Oxygen uptake rates (OUR) of MBR sludges were determined within the biological reactors. For this purpose the sludge was aerated to a DO of approximately 8 mg L^{-1}. Aeration was subsequently stopped and DO decrease was followed in time with a portable DO sensor (Hach Lange). Slow mechanical mixing of the reactor contents was performed to prevent sludge settling. The OUR was calculated from the maximum slope of the decrease in DO in time. Additional batch OUR tests with 200 mL of 24 h pre-aerated sludge and 100 mL of NF concentrate were performed to investigate biodegradability and toxicity of the concentrate. After aeration to a maximum DO (approximately 8 mg L^{-1}), the decrease of the DO was followed in time. After a second aeration phase to a maximum DO, 100 mL NF concentrate was added and the procedure was repeated. Finally, in a similar manner occasional batch OUR tests were performed at an ammonium and acetate concentrations respectively of 195 mg NH_4-N L^{-1} and 550 mg COD L^{-1} of acetate, both in the presence as well as in the absence of 5 mg L^{-1} of copper.

Oxygen transfer coefficients were determined with 0.5 L sludge samples in batch tests under endogenous respiration conditions, following the method described by [17]. One liter beakers were used and were aerated with a fish tank aerator at an air flow rate of 0.6 L h^{-1}. The beakers were mixed with a magnetic stirrer at room temperature. Dissolved oxygen concentration was followed in time by a handheld DO meter (Hach Lange).

Floc strength was assessed qualitatively by determining turbidity in sludge supernatants before and after exposing the sludge to additional shear stress. For this purpose a 400 mL sludge sample was taken from the reactor. Of this sludge, 200 mL was centrifuged immediately for one minute at 700 rpm (Alegra x-12R, Beckman Coulter Inc.) after which the turbidity of the supernatant was immediately determined by a turbidity meter (2100N IS, Hach-Lange). To apply shear stress the other 200 mL of sludge was transferred to a 1,000 mL beaker and stirred for 20 minutes at 700 rpm with a magnetic stirrer (stirring bar of 5 cm length). Directly after these 20 minutes the sample was centrifuged at 700 rpm for 1 minute and the turbidity of the supernatant was measured.

3.3. Results

The first 100 days of MBR operation with and without NF concentrate recirculation were considered as a startup phase and the data obtained during this period were discarded. Reported average concentrations between days 100 and 220 are all based on 20 to 30 grab samples taken twice a week over this period. The relatively high standard deviations were mainly caused by time-varying fluctuations in composition and concentration of the wastewater that was used.

3.3.1 COD removal

Average COD concentrations of pre-settled wastewater, both MBR permeates and NF concentrate between days 100 and 220 are presented in Table 3.2. The average BOD_5/COD ratio of the wastewater was 0.33 ± 0.09. Overall COD removal efficiencies were 99% for the R100% MBR NF combination and 93% for the R0% MBR. Corresponding effluent COD concentrations of the two treatment systems were 27 ± 5 (R0%) and 3 ± 3 mg L^{-1} (R100%), indicating a better reuse potential of the water that was produced by the combined MBR NF system. The measured COD concentration of the NF concentrate of 80 ± 18 mg L^{-1} was much lower than a concentration of 198 mg L^{-1}, calculated from COD rejection by the NF membrane of 92% (Table 3.1). The reason for this will be discussed in more detail later on when the COD mass balances for the two treatment systems are described.

Table 3.2 *Average COD concentrations of pre-settled wastewater, MBR permeates and NF concentrate and permeate between days 100 and 220 (20-30 samples).*

Source	Sample	COD concentration ($mg L^{-1}$)
Pre-settled wastewater	Total	403 ± 107
	Suspended	209 ± 35
	Colloidal	85 ± 24
	Dissolved	109 ± 48
R0%	MBR permeate	27 ± 5
R100%	MBR permeate	39 ± 8
	NF permeate	3 ± 3
	NF concentrate	80 ± 18

Although the average colloidal COD concentration in R100% (20 ± 16 mg L^{-1}) generally was higher than in R0% (15 ± 10 mg L^{-1}), it was not possible to detect a clear and consistent difference between the two reactors. In contrast, as shown in Fig. 3.2a, the dissolved COD concentrations were consistently higher in R100% (69 ± 13 mg L^{-1}) than those in R0% (55 ± 8 mg L^{-1}). Occasional analyses of humic acids by LC-OCD in 0.45 µm filtered sludge samples showed that also concentrations of humic acids in R100% (20 ± 6 mg L^{-1}) generally were higher than in R0% (15 ± 4 mg L^{-1}).

Due to the higher concentrations of dissolved and colloidal COD in R100% compared to R0%, it can be expected that fouling of the R100% membranes was more severe. This indeed was the case because after each physical and chemical membrane cleaning the membranes in R100% always reached the maximum permitted TMP of 400 mbar before this occurred for the R0% membranes. This was also confirmed by additional filtration experiments with the different fractions of the sludges from these reactors, reported by [15]. These data showed that not the high concentration of suspended solids but rather the higher COD in the supernatant dominated fouling of the MBR membranes, especially in R100%. More details on the fouling behavior of the MBR membranes can be found in [15].

Similar to dissolved COD concentrations in the MBR reactors, also COD concentrations in R100% MBR permeate were consistently higher than those in R0% permeate (Fig. 3.2b), with average concentrations of 39 ± 8 mg L^{-1} and 27 ± 5 mg L^{-1}, respectively (Table 3.2).

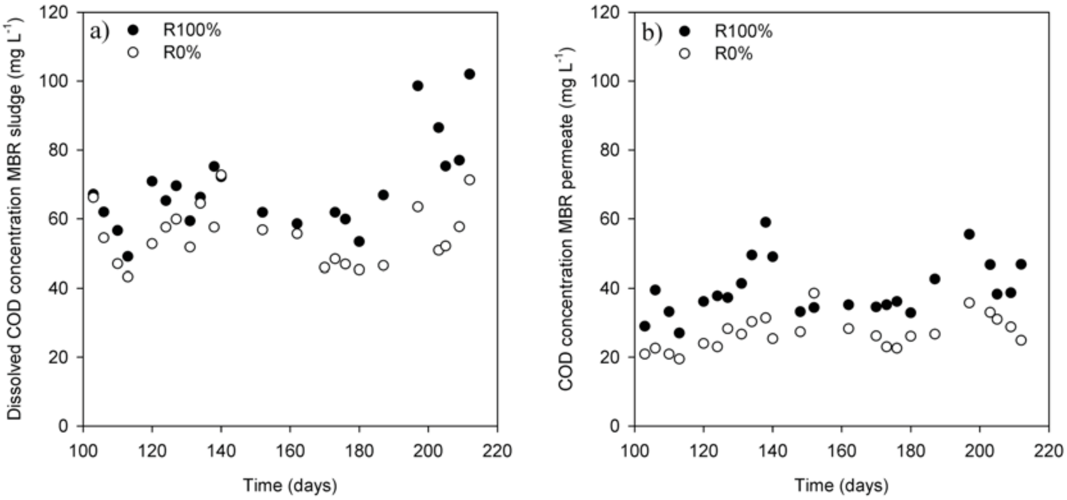


Fig. 3.2 *Dissolved COD concentrations in a) MBR reactors and b) in permeate of MBR reactors.*

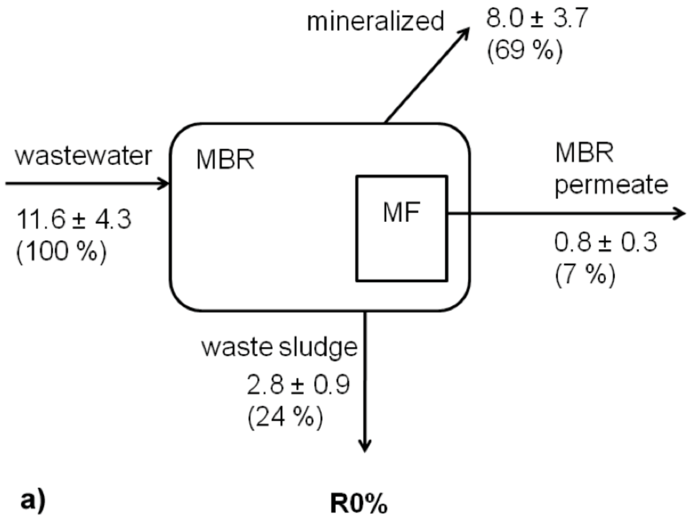
Rejection of dissolved COD by the MBR microfiltration membranes was 43% in R100% and 51% in R0%. Average dissolved COD concentrations in the R100% MBR reactor and permeate were 12-14 mg L^{-1} higher than their respective concentrations in the R0% system. This difference corresponds very well to the additional dissolved COD concentration of 12 mg L^{-1} resulting from the NF concentrate recirculation received by R100%. Apparently the COD in the NF concentrate is non-biodegradable, is not adsorbed by the sludge, is not rejected by the (microfiltration) MBR membranes, but is fully rejected by the NF membrane. The absence of readily biodegradable COD in the NF concentrate was confirmed by OUR determination in batch tests with MBR sludge, which did not give an increase in OUR when NF concentrate was added (data not shown).

3.3.2 Mineralization and sludge production

Fig. 3.3 presents COD mass balances for the R0% MBR and R100% MBR NF system, expressed in gCOD day^{-1} and as a percentage of the wastewater COD load. The mineralized COD load was calculated as the mass balance closure around the MBR reactors.

The mass balance around the NF setup in the R100% MBR NF system showed a discrepancy of approximately 0.8 gCOD day^{-1} (6.8% of the wastewater COD load) between the load of COD that was fed to the NF and the sum of the NF concentrate and NF permeate COD load. Partly, this gap in may be attributed to fouling of the NF membrane, which was not accounted for in the mass balance because after each NF concentrate production cycle (every two weeks) fouling was removed and discarded. Recalculated with a measured COD/TOC ratio of 2.3 in

R100% MBR permeate, a fouling between 0.02 and 0.14 mgCOD cm^{-2} of membrane area was found during a NF membrane autopsy performed after one concentrate production cycle [15]. This however only corresponds to a COD load of 0.04-0.26 gCOD day^{-1}, not explaining the mass balance gap of 0.8 gCOD day^{-1}. Other factors contributing to the gap in the mass balance are variations in NF permeate concentration. For practical reasons only three grab samples were taken from the NF permeate. As rejection changes with feed concentration, the concentration in the NF permeate may have been periodically higher. Finally, water remaining inside the NF unit after the concentrate production could not be taken into account and therefore the concentration factors were slightly lower (10%) than they should have been. All this may have contributed to the gap in the NF mass balance.



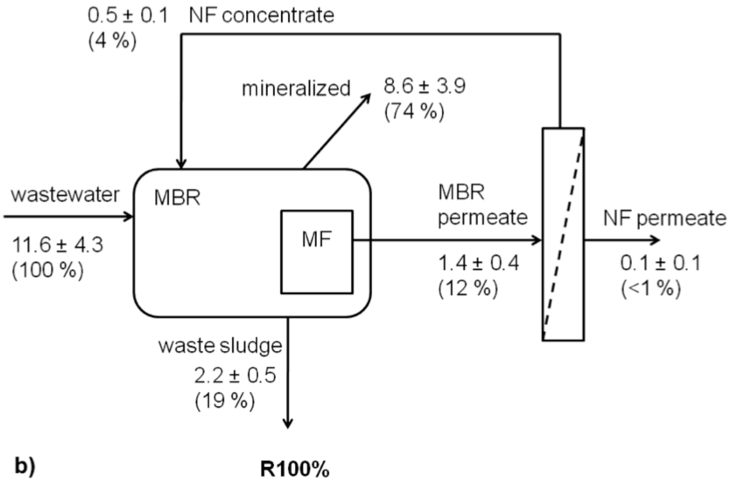


Fig. 3.3 *COD mass balances in a) R0% MBR and b) R100% MBR NF system. Values represent COD mass loads in gCOD* day^{-1} *and percentages of the wastewater COD load.*

Comparing the COD mass balances of the two MBRs (Fig. 3.3), it appears that the additional NF concentrate COD load on the R100% MBR resulted in a similarly higher COD load in the permeate of this MBR. This was already explained previously and strongly suggests that the organic compounds in the NF concentrate had a non-biodegradable character, did not adsorb to the sludge flocs and were not rejected by the 0.4 µm MBR membranes.

From the COD load that was discharged with the MBR excess sludge, average sludge yields were calculated for R0% of 0.27 ± 0.08 gCOD $gCOD^{-1}$ (0.16 ± 0.07 gVSS $gCOD_{removed}^{-1}$) and for R100% of 0.22 ± 0.08 gCOD $gCOD_{removed}^{-1}$ (0.13 ± 0.05 gVSS $gCOD_{removed}^{-1}$). These yields are very low, which was probably caused by the relatively high biodegradability of the wastewater (BOD_5/COD ratio of 0.33 ± 0.09) and a relatively high water temperature during the experimental period of 16.7 ± 2.1 ˚C. As a result, also the average sludge concentrations of 3.5-4.5 gTSS L^{-1} (Table 3.5) were on the lower end compared to typical sludge concentrations of 3.6-18.3 gTSS L^{-1} in full scale MBRs treating municipal wastewaters [18].

The fraction of oxidized wastewater COD was calculated from the COD mass balance closures around the MBR (Fig. 3.3). From the lower (net) sludge yield in R100% it follows that in R100% more COD was oxidized (74%) compared to R0% (69%). These differences were unexpected because the MBR reactors were operated at the same SRT of 16 days. Similar experiments, in which the reactors were operated over another 200 days showed exactly the same trend (data not shown). Theoretically, more mineralization of organic matter should be accompanied by more oxygen consumption. However, occasional OUR measurements showed that the OUR in R100% was 10-25% lower than in R0%. Also the observation that, at identical air flow rates, the DO concentrations in R100% (3.2 ± 2.5 mg L^{-1}) always exceeded those in R0% (2.2 ± 2.5 mg L^{-1}) does not agree with more COD oxidation in R100%. Remark that this difference in DO cannot be explained by differences in oxygen transfer rate because separate measurements of this rate gave similar results for the two reactors.

3.3.3 Nitrogen and phosphorous

Table 3.3 gives average concentrations of nitrogen and phosphorus of the (pre-settled) wastewater, both MBR permeates, NF concentrate and NF permeate.

***Table 3.3** Average nitrogen and phosphorus concentrations of (pre-settled) wastewater, both MBR permeates and of R100% NF concentrate and permeate between days 100 and 220 (based on 20-30 grab samples).*

			R0% MBR	R100% MBR NF		
parameter	unit	pre-settled wastewater	MBR permeate	MBR permeate	NF concentrate	NF permeate
total N	mg N L^{-1}	51 ± 14	32 ± 12	41 ± 7	45 ± 10	32 ± 1
NH_4-N	mg N L^{-1}	38 ± 10	7 ± 8	2 ± 4	< 0.1	< 0.1
NO_3-N	mg N L^{-1}	< 0.3	21 ± 14	34 ± 7	38 ± 11	32 ± 7
Total P	mg P L^{-1}	7.1 ± 3.2	6.5 ± 1.6	6.7 ± 1.0	7.9 ± 1.9	0.2 ± 0.1
PO_4-P	mg P L^{-1}	5.0 ± 1.9	5.5 ± 1.8	5.8 ± 1.1	7.1 ± 1.8	0.10 ± 0.05

In both MBRs ammonium removal efficiencies generally exceeded 95%, although in particular in R0% operational problems occasionally caused significantly lower efficiencies. This also explains the higher average ammonium concentration in the permeate of R0% (7 ± 8 mg NH_4-N L^{-1}) compared to R100% (2 ± 4 mg NH_4-N L^{-1}). However, the observation that similarly high ammonium removal efficiencies could be accomplished in R0% and R100% demonstrates that full recirculation of NF concentrate to R100% did not result in inhibition of the nitrification process.

As the MBR systems were not designed to accommodate denitrification, the permeate of R0% contained a high nitrate concentration of 21 ± 14 mg NO_3-N L^{-1}. The nitrate concentration of the R100% MBR permeate was even higher (34 ± 7 mg NO_3-N L^{-1}), which mainly can be attributed to the higher average nitrification efficiency of R100%. To a small degree the higher nitrate concentration in R100% permeate can also be explained by the nitrate rejection of 6% by the NF membrane. Such a low rejection of nitrate by the NF270 membranes was also found by others for synthetic salt solutions using the same membrane [19, 20]. The lower sludge production in R100% may also have contributed to a higher nitrate concentration in the MBR permeate because this is accompanied by a lower ammonium uptake by (heterotrophic) biomass and thus by more ammonium that is available for nitrification to nitrate. The same phenomena can also explain the differences that were found between total nitrogen concentrations of R0% and R100% permeates.

Similar to denitrification, the treatment systems were not designed for biological or chemical phosphorus removal. Phosphorus was only removed by 11-12% by subsequent biomass uptake and excess sludge production. Phosphate concentrations in the MBR permeates were even slightly higher than in the wastewater, probably because part of the organically bound phosphorus was solubilized into phosphate. Obviously, because of the high phosphate rejection by the NF membrane of 99% (Table 3.1), the R100% MBR NF system produced a much better effluent quality with respect to phosphorus than the R0% MBR system (Table 3.3). However, the phosphate concentration in the NF concentrate was much lower than what was expected from the 99% phosphate rejection by the NF membrane. Approximately 80% of the phosphate in R100% precipitated during NF treatment and was removed from the system after citric acid cleaning. This was accompanied by severe calcium phosphate scaling of the NF membrane [15].

A similar phenomenon was also observed during combined MBR RO treatment of municipal wastewater [2]. This suggests that recovery of phosphorous from the NF concentrate loop not only can improve NF operation but also may generate a valuable phosphorus product.

3.3.4 Heavy metals

Of the heavy metals, only copper could be determined in a reliable manner, mainly because concentrations of the other metals generally were found to be below their method detection limits. Concentrations of copper are given in Table 3.4.

Table 3.4 *Average copper concentrations of pre-settled wastewater, both MBR permeates and of R100% NF concentrate and permeate between days 100 and 220 (based on 20-30 samples). The wastewater concentration is the total copper concentration and the other concentrations reflect are in 0.45 µm filtered samples.*

parameter	unit	pre-settled wastewater	R0% MBR permeate	R100% MBR NF MBR permeate	R100% MBR NF NF concentrate	R100% MBR NF NF permeate
Cu	mg L^{-1}	0.61 ± 0.09	0.49 ± 0.34	0.52 ± 0.25	0.60 ± 0.25	0.11 ± 0.05

The rejection of copper by the NF membrane was 79% (Table 3.1) and due to recirculation of rejected copper much higher concentrations were therefore expected in R100% than in R0%. The mass balance closure for copper around both MBR systems was close to 100%. However, a mass balance calculation around the NF setup showed that 75% of the copper that was rejected by the NF membrane did not appear as dissolved copper in the concentrate. Earlier, an autopsy showed that copper was part of the NF membrane scaling [15] and a substantial amount of copper probably was discarded with the NF fouling after citric acid cleaning. Nevertheless, recirculation of the remaining copper in the NF concentrate (0.60 ± 0.25 mg L^{-1}) still resulted in a slightly higher R100% permeate concentration (0.52 ± 0.25 mg L^{-1}) in R100% permeate compared to R0% permeate (0.49 ± 0.34 mg L^{-1}). Also the average adsorbed concentration of copper in sludge of R100% (2.0 ± 0.6 mg g^{-1} TSS) was higher than that of R0% (1.8 ± 0.5 mg g^{-1} TSS).

Similar to copper, also other metals were largely rejected by the NF membranes. In the NF permeate aluminum and zinc for example were always below their method detection limits of 50 and 25 μg L^{-1}, respectively. It can therefore be expected that also other heavy metals are present at higher concentrations in R100% than in R0%. For aluminum and iron this could be verified by determining the metal content of the sludge. The values found for aluminum were 3.8 ± 1.4 and 3.5 ± 1.2 mg g^{-1} TSS and for iron 8.0 ± 2.4 and 7.1 ± 1.6 mg g^{-1} TSS, respectively for R100% and R0% sludge. In spite of the higher (heavy) metal concentrations in R100% this apparently did not have a negative (toxic) effect on biological COD removal and nitrification as the performance of these processes was similar for both MBRs. This was further supported by OUR tests, where the addition of an approximately 10 times higher copper concentration of 5 mg L^{-1} to R0% and R100% sludge did not negatively impact acetate and ammonium oxidation (data not shown).

3.3.5 Sludge properties

Several properties of R0% and R100% sludges are presented in Table 3.5.

***Table 3.5** Average sludge properties based on 20-30 grab samples taken between days 100 and 220.*

property	unit	R0%	R100%
TSS	g L^{-1}	4.5 ± 0.9	3.5 ± 0.9
VSS	g L^{-1}	3.6 ± 0.8	2.8 ± 0.7
ash content	%	20 ± 2	21 ± 2
N content	mg N $gVSS^{-1}$	102 ± 38	110 ± 19
P content	mg P $gVSS^{-1}$	20 ± 3	23 ± 6
Ca content	mg Ca $gTSS^{-1}$	33 ± 6	39 ± 11
Mg content	mg Mg $gTSS^{-1}$	3.8 ± 0.8	4.2 ± 1.2
SVI	mL $gTSS^{-1}$	96 ± 54	75 ± 41

As described earlier, the sludge yield of R100% was lower than of R0% and thus also the average sludge concentration: 3.5 ± 0.9 g TSS L^{-1} and 2.8 ± 0.8 g VSS L^{-1} in R100% versus

4.5 ± 0.9 g TSS L^{-1} and 3.6 ± 0.8 g VSS L^{-1} in R0% (Table 3.5). The nitrogen and phosphorus contents of the two sludges were similar (102-110 mg N $gVSS^{-1}$ and 20-23 mg P $gVSS^{-1}$) and are in line with values that are normally found in the waste sludge of biological treatment plants.

The ash content was slightly but consistently higher in R100% (21 ± 2%) than in R0% sludge (20 ± 2%). This can be attributed to the additional load of multivalent cations resulting from NF concentrate recirculation in R100%, leading to higher concentrations of inorganic species such as calcium, magnesium iron, aluminum and copper. These ions may have formed precipitates or were bound by sludge extracellular polymers [13, 21].

Fig. 3.4 shows representative examples of microscopic images of sludge flocs in R0% and R100%, taken on day 204. The sludge flocs in R100% always were more compact than the sludge flocs in R0%. This could indicate that they were more resistant against shear than the flocs in R0%. To test this hypothesis several shear test were performed. With both sludges the additional shear (20 minutes at 700 rpm with a 5 cm stirring rod) caused an increase in turbidity. This turbidity increase was always most pronounced with sludge of R0%. Typically, R0% sludge gave a turbidity increase of 35-65% whereas R100% sludge resulted in a lower turbidity increase of 29-48%. This confirms that the sludge flocs in R0% were more prone to shear than the sludge flocs in R0%.

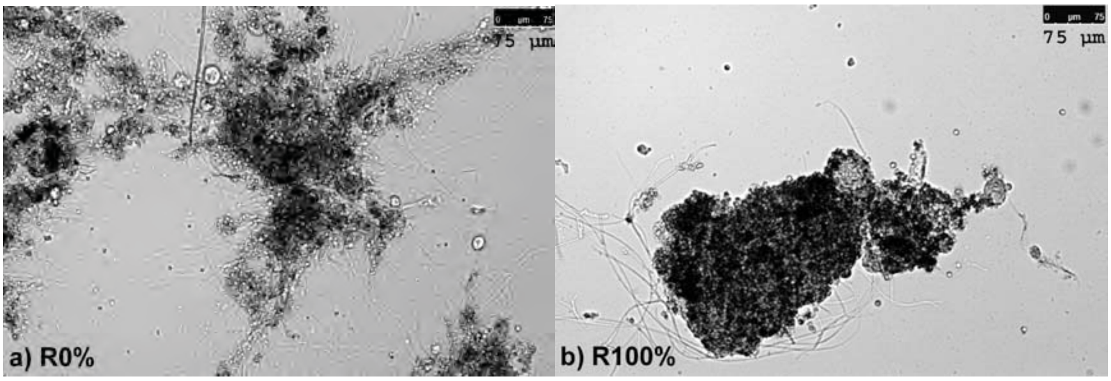


Fig. 3.4 *Representative light microscopic images of a) R0% and b) R100% sludge samples taken after 204 days of operation.*

The stronger flocs in R100% may have been the result of higher concentrations of calcium, magnesium and iron in the sludge of R100% because these cations supposedly are responsible for bridging the extracellular polymers that help to aggregate microorganisms and wastewater particles and to maintain the structure of the sludge flocs [22-24]. The NF membrane exhibited a high rejection of multivalent cations (Table 3.1) and Table 3.5 shows this also resulted in somewhat higher concentrations of these elements in the sludge of R100% than in the sludge of R0%.

Similarly, a good flocculation process and the formation of strong sludge flocs often are related to a mono- to divalent cation ratio (M/D) in the feed below 2 [21, 25]. If this ratio is too high, monovalent cations start replacing multivalent cations in the sludge matrix and this could lead to reduced floc strength and poor flocculation. Table 3.6 gives measured dissolved concentrations of the dominant monovalent ions (Na and K) and multivalent ions (Ca and Mg) in the wastewater and in the NF concentrate. The contribution of other cations was found to be negligible.

Table 3.6 *Dissolved mono- and divalent cation concentrations and monovalent to divalent cation ratio (M/D) in pre-settled wastewater, NF concentrate and R100% feed.*

Ion	Unit	Pre-settled wastewater [*]	NF concentrate	R100% feed
Na^+	mg L^{-1}	137 ± 28	176 ± 16	146 ± 24
K^+	mg L^{-1}	22 ± 4	31 ± 2	24 ± 3
Ca^{2+}	mg L^{-1}	68 ± 8	131 ± 10	81 ± 7
Mg^{2+}	mg L^{-1}	18 ± 5	44 ± 7	23 ± 4
M/D	eq eq^{-1}	1.34 ± 0.32	0.83 ± 0.20	1.17 ± 0.31

[*] equivalent to R0% feed

The ion composition of the NF concentrate was in line with the high rejections of the NF membrane for multivalent cations and much lower rejections for monovalent ions (Table 3.1). From the measured concentrations, those in the combined wastewater and NF concentrate feed of R100% were calculated, as well as the M/D ratios in these streams (Table 3.6). These values show that due to full NF concentrate recirculation the M/D ratio in the feed of R100% (1.17 eq eq^{-1}) was somewhat lower than the M/D ratio of the wastewater, i.e. the feed of R0% (1.34 eq eq^{-1}). This lower M/D ratio in the feed of R100% may have had a positive effect on flocculation, even though Higgins et al. mentioned that only M/D ratio's exceeding 2 will result in serious flocculation problems [21, 25].

Although not directly relevant for MBR systems, sludge settleability was determined as another indication of the quality of sludge flocculation. The SVI of both sludges was highly variable, but a significant and consistently lower average SVI was found for R100% sludge (75 ± 41 mL $gTSS^{-1}$) than for R0% sludge (96 ± 54 mL $gTSS^{-1}$). During the last 50-75 days of operation this difference was even more pronounced with SVI values for R0% always exceeding 120 mL $gTSS^{-1}$ and very stable values for R100% below 60 mL $gTSS^{-1}$. Such an improved settleability in relation to a lower M/D ratio was also described by [26].

Well flocculating sludge and/or a high resistance against shear are often mentioned as a prerequisite for a sustainable and robust membrane filtration process [27]. The results of the shear tests, the presence of higher concentrations of multivalent cations in the sludge, a lower M/D ratio of the feed and an improved settleability all pointed towards better flocculation upon NF concentrate recirculation in R100%. However, we observed the opposite from the TMP data and critical flux measurements: the filterability of R100% sludge was worse than of R0% sludge [15]. Most likely this was caused by the presence of higher concentrations of (non-biodegradable) dissolved COD in R100% (Fig. 3.2a) or by the more compact sludge flocs in R100% (Fig. 4b) having a lower capacity to capture the colloidal COD coming in with the wastewater. This is in agreement with observations by [15] that the low concentrations of dissolved and colloidal matter rather than the high concentrations of suspended matter dominated fouling of the MBR microfiltration membranes.

3.4. Discussion

3.4.1 Biodegradation of organic compounds

Recirculation of NF concentrate to an MBR prolongs the biological contact time of those (dissolved) organic compounds that are rejected by the NF membrane. This could make these compounds more vulnerable to biodegradation. Indeed, an improved biodegradation was observed [12] in a MBR RO system with (partial) RO concentrate recirculation, treating a mixture of 40% municipal and 60% industrial wastewater. Also others claimed an enhanced biodegradation of slowly biodegradable organic compounds when they applied NF concentrate recirculation to a MBR that was fed with tannery and textile wastewater [11]. In our experiments with municipal wastewater treatment by a combined MBR NF system with full NF concentrate recirculation, evidence for such an improved biodegradation of (soluble) organic compounds in the NF concentrate was not found, even after an acclimation period of 220 days. The COD concentration in R100% permeate possibly was higher due to recirculation of non-biodegradable organics (possibly humic acids) that originated from the wastewater. Because of the lower sludge production of R100%, in this reactor also biological decay products may have been present at elevated concentrations. However, this does not exclude the possibility that some micropollutants such as personal care product and medicines, present in municipal wastewaters in the ng - μg L^{-1} range, are more efficiently removed due to NF concentrate recirculation [2].

Although an improved biodegradation of organic compounds in the NF concentrate was not observed, the sludge yield in the R100% MBR with full NF concentrate recirculation (0.13 gVSS $gCOD_{removed}^{-1}$) was significantly lower than in the R0% MBR without NF concentrate recirculation (0.16 gVSS $gCOD_{removed}^{-1}$). Although this could not be confirmed by measurements of the oxygen consumption rate, this must have been accompanied by more COD oxidation in R100% (74%) than in R0% (69%) (Fig. 3.3). The reason for a reduced yield and more COD oxidation is unknown. One possible reason for more COD oxidation and a lower sludge production can be sludge grazing by protozoa and other higher organisms [28]. However, although this cannot be entirely excluded, frequent microscopic inspection did not reveal the presence of more protozoa and other higher organisms in R100% sludge than in R0% sludge. Another explanation may be recirculation of heavy metals or organic compounds such as humics, antibiotics or other medicines with the NF concentrate which uncouple phosphorylation in the sludge bacteria [29-31] or compounds which enhance cell death and lysis. It remains unclear which specific compounds were present at sufficiently high concentration in R100% to achieve such an effect.

3.4.2 Absence of toxicity for nitrification

A comparison with R0% revealed that recirculation of NF concentrate did not have a negative impact on the nitrification performance of R100%. One reason for toxicity could have been the expected accumulation of heavy metals that are known to inhibit nitrification already at low concentrations [32]. A mass balance showed that a large fraction of copper (80%), and presumably also of other heavy metals, was wasted from the system during the production of NF concentrate and was not recirculated to R100%. When all the copper that was rejected by the NF would have been recirculated to R100%, this would have given an approximate 1.5-2 times higher (total) copper concentration in R100% compared to R0%. Still, OUR tests where 10 times higher copper concentrations were added to batches of nitrifying sludge, did not exhibit any negative effect on the OUR compared to tests in the absence of copper. We therefore do not expect that full recirculation of heavy metals such as copper will present serious toxicity problems although long-term effects cannot be excluded.

3.4.3 Feasibility of NF concentrate recirculation

With respect to biological COD removal and nitrification, NF concentrate recirculation certainly is feasible because these processes were not hampered. In addition, NF recirculation resulted in a 21% lower sludge production, which can reduce the sludge treatment costs. These treatment costs are partly determined by dewatering. The settleability of R100% sludge was much better than of R0% sludge and even though no dewaterability experiments were performed, this provides an indication that also the sludge dewaterability of R100% sludge may be better than of R0% sludge. This is in agreement with [33] who reported that higher multivalent cation concentrations improve sludge dewaterability. Membrane fouling was more severe in R100% than in R0%, mainly caused by the presence of higher concentrations of (dissolved) COD in R100%. The impact of this on membrane operational costs still needs to be further evaluated.

The main bottleneck of the combined MBR NF recirculation system therefore is membrane fouling, not only of the MBR membranes, but in particular of the NF membrane. Inorganic scaling of the NF membrane mainly caused by calcium phosphates, was found to be the dominant fouling process and should be solved before a practical application of the full NF concentrate recirculation is feasible [15]. Electrochemical technology as proposed by [10] or other phosphate recovery technologies could be used to recover phosphate, not only because this helps to relieve the pressure on scarce natural phosphorus reserves, but also because this would reduces NF scaling. However, it is recognized that this phosphate recovery probably will be accompanied by removal of heavy metals and questions remain regarding the quality of the phosphorus product that will be obtained in this manner.

3.5 Conclusions

Recirculation of NF concentrate to an MBR did not have a negative impact on COD removal and nitrification in this MBR. A combined MBR NF system with concentrate recirculation therefore provides a more sustainable alternative for systems where the NF concentrate is simply discharged as a waste stream to the environment. An additional advantage is that concentrate recirculation reduced the sludge production in comparison with an MBR which did not receive NF concentrate. Although concentrate recirculation resulted in improved sludge flocculation, fouling of the MBR membranes was more severe due to recirculation of higher concentrations of (soluble) non-biodegradable organic compounds. Finally, calcium phosphate precipitation and scaling of the NF membrane is accompanied by removal of a large fraction of the heavy metals present in the MBR permeate. This should be taken into account when phosphate recovery is applied because this will affect the quality of the phosphorus product.

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4

Impacts of NF concentrate recirculation on membrane performance in an integrated MBR and NF membrane process for wastewater treatment

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Abstract

As water shortages are increasing, the need for sustainable water treatment and the reuse of water is essential. Water reuse from wastewater can be accomplished in a membrane bioreactor (MBR) in the secondary activated sludge stage of a wastewater treatment plant. To remove viruses, dissolved organics and inorganics still present in the MBR permeate, nanofiltration (NF) can be applied. Nevertheless, the major drawback of nanofiltration membranes is the production of a concentrate stream that cannot be discharged to the environment. In this research we investigate the concept of a combined MBR and NF system with NF concentrate recirculation back to the MBR to produce reusable water in a sustainable way. Long-term continuous operation (1 year) shows that the NF permeate quality is not impacted by the recirculation. Fouling on the NF membrane is mostly the result of inorganics, while organics (e.g. humic acids) do not have a major impact on NF fouling. In fact, the flux of the NF was enhanced by the presence of humic acids due to recirculation. However, the MBR showed increased fouling and consequently more frequent membrane cleaning. The results presented show that the continuous production of reusable water from wastewater in a combined MBR and NF process with NF concentrate recirculation can be successful.

4.1. Introduction

As fresh water shortages are increasing, the need for sustainable water treatment processes has become essential. For example, water reuse from municipal wastewater could be accomplished by a membrane bioreactor (MBR) for combined biological and membrane treatment. Commonly, micro- (MF) or ultrafiltration (UF) membranes are applied to separate solids (biological sludge) from the treated water phase and in this manner deliver a high quality and solids free permeate. However, MBR permeate can still contain viruses and dissolved organic pollutants that have to be removed before the water can be reused. This can be accomplished by dense membrane processes such as nanofiltration (NF) or reverse osmosis (RO). NF produces a very high quality permeate that is ready for reuse for instance for irrigation or industrial applications such as cooling water [1]. Although RO membranes would give the highest permeate quality, their high salt retention compared to NF would result in a strong increase in salinity in the MBR. This could be harmful to the bacteria because increased osmotic pressure damages bacterial cell walls. Also from an energetic point of view, RO generally would be less favorable than NF due to the higher applied feed pressures required. However, the major drawback of nanofiltration is the production of a concentrate stream, which can have a volume up to 10-20% of the wastewater volume.

NF concentrate can also be considered a resource for the recovery of valuable compounds like phosphates, although this would require additional technology [2]. Depending on the wastewater constituents, which to a certain extent are rejected by NF, the concentrate cannot be simply discharged to the environment because it contains heavy metals and organic micropollutants, which are harmful for aquatic organisms [3]. A possible strategy to avoid this, is to recirculate the NF concentrate to the preceding MBR system [4, 5].

Combined MBR and NF treatment of wastewaters is already described in the literature [4]. However, the impacts of (full) recirculation of untreated NF concentrate on the biological MBR processes and on MBR and NF membrane performance have not yet been investigated. The prolonged (biological) contact time caused by concentrate recirculation may stimulate the biodegradation of some of the organic micropollutants such as pharmaceuticals and personal care products [6]. However, as organics are known to foul NF membrane [7], the recirculation of non-biodegradable organic matter could also directly or indirectly contribute to membrane fouling.

Since rejection of micropollutants by NF is high, NF concentrate recirculation will yield higher multivalent cation concentrations in the MBR. Especially increased calcium, but also magnesium and iron concentrations, are known to reduce the fouling potential in MBRs [8, 9] because they promote bioflocculation. However, when concentrations of multivalent ions become too high, this may induce scaling of the membrane.

The aim of this study was to investigate the impact of concentrate recirculation in a combined MBR and NF process (MBR NF) on the performance of the MBR and NF membranes in more detail, and to evaluate the feasibility of this integrated concept for production of reusable water. For this purpose two MBR systems were operated in parallel for 364 days. The permeate of one MBR was treated by nanofiltration (NF) and the NF concentrate was recirculated to this MBR. The other MBR without NF concentrate recirculation served as a blank system. Differences between the two systems in terms of transmembrane pressure (TMP), critical flux, membrane resistances, membrane rejections of specific constituents, contributions to fouling by scaling and organic fouling were all investigated, and the effect of the pH on these was determined as well. Also NF membrane autopsies in an early and a later stage of the operation were carried out. The main foulants were identified by dedicated dead-end filtration tests with MBR sludge and MBR supernatants.

4.2. Experimental setups

4.2.1 Lab scale MBR and NF setup

To determine the effect of NF concentrate recirculation on the MBR process, two seven-liter lab scale MBR units were operated for 364 days. Both reactors were aerated with coarse bubble aeration plates at an average airflow rate of 0.6 m^3 m^{-2} h^{-1} for biological as well as membrane aeration. Municipal wastewater from a nearby sewer system was pre-settled and fed to both reactors at a flow rate of 36 L day^{-1} (Fig. 4.1). Wastewater characteristics are shown in Table 4.1.

Table 4.1. *Wastewater characteristics (mg L^{-1}) in terms of COD and its fractions as well as elements and anions measured in the dissolved phase.*

	unit			**unit**	
COD total	mg O_2 L^{-1}	403 ± 107	**TC**	mg L^{-1}	137 ± 22
COD suspended	mg O_2 L^{-1}	209 ± 35	**TIC**	mg L^{-1}	93.3 ± 9.6
COD colloidal	mg O_2 L^{-1}	85 ± 24	**TOC**	mg L^{-1}	42.4 ± 17.8
COD dissolved	mg O_2 L^{-1}	109 ± 48	**Calcium**	mg L^{-1}	68.2 ± 7.5
NH_4-N	mg L^{-1}	38.1 ± 9.8	**Magnesium**	mg L^{-1}	18.0 ± 4.7
NO_3-N	mg L^{-1}	< 0.3	**Silicon**	mg L^{-1}	15.3 ± 1.4
Copper	mg L^{-1}	0.55 ± 0.22	**Sulphur**	mg L^{-1}	2.3 ± 8.0
Potassium	mg L^{-1}	21.6 ± 3.6	**Chloride**	mg L^{-1}	177 ± 62
Phosphorous	mg L^{-1}	6.0 ± 1.8	**Sodium**	mg L^{-1}	137 ± 28

Each MBR contained two submerged MF flat sheet membranes (Kubota, Japan) with a surface area of 0.116 m^2 per plate and 0.4 μm pore size. The membranes were operated at a flux of 6.4-7.5 L m^{-2} hr^{-1} (LMH). Membrane relaxation steps of two minutes were performed every eight minutes.

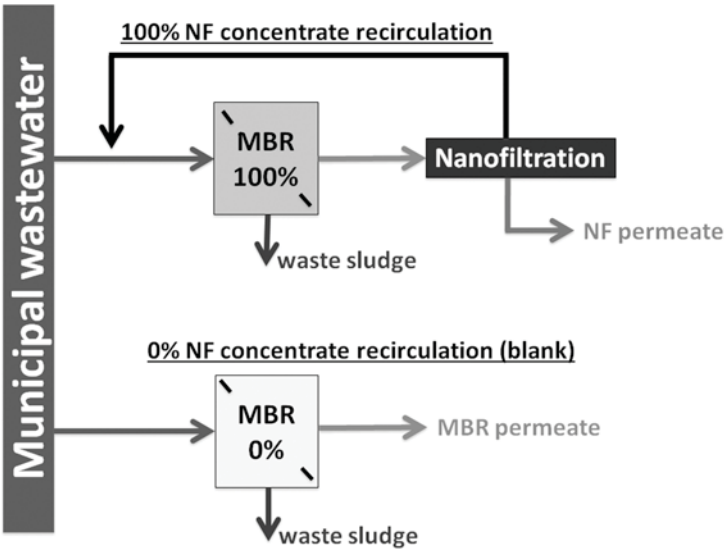

Fig. 4.1. *Lab-scale MBR systems without (R0%) and with full (R100%) NF concentrate recycling.*

One MBR system (R0%) served as a control system without NF concentrate recirculation and the permeate was discharged into the sewer system. The other MBR (R100%) was also fed with the pre-settled wastewater and additionally with NF concentrate. For this purpose 600 L R100% MBR permeate was collected in time during two weeks, stored at room temperature, and every two weeks batch wise concentrated down to 100 L. For this, a lab-scale nanofiltration setup containing a 2.5’’ spiral-wound NF270 module (DOW) was used. A maximum permeate recovery of around 85% was achieved. This concentrate production was carried out at 11 bar. After each cycle of concentrate production, a chemical cleaning of the 2.5’’ module was performed at a pressure of 2 bar. The module was rinsed with citric acid at pH 4 for 10 minutes, followed by a rinse with tap water for 10 minutes.

The 100 L of concentrate was fed continuously at a flow rate of 6.48 L day^{-1} to the R100% MBR, additionally to the pre-settled wastewater. The NF concentrate represented 15% of the total inflow (wastewater + concentrate) and the wastewater the other 85%.

Temperature, pH, hydraulic retention time (HRT), solids retention time (SRT) as well as the dissolved oxygen concentration in both MBR systems were equal. The temperature and pH in the MBRs were not controlled but remained constant around 16.7 ± 2.1 ˚C and 7.5 ± 0.2, respectively. HRT and SRT were set to 4.7 hours and 16 days, respectively. Dissolved oxygen concentration in the reactors was kept around 1-4 mg L^{-1} by manual control of the airflow rate. The airflow rate was varying in time (also depending on the strength of the wastewater) but was always kept equal in both reactors to assure equal shear. The TMP was recorded with pressure sensors (Endress + Hauser, Cerabar M). When the TMP of one of the MBR membranes exceeded 400 mbar, all membranes in the two reactors were cleaned. As this was determined by the R100% MBR in this research (which showed the most severe fouling), cleaning needed to be done twice a month. The membranes were taken out of the reactors, cleaned physically with a sponge, followed by chemical cleaning for 4 hours: soaking in 0.2 g L^{-1} sodium-hypochlorite (NaOCl) for 2 hours, followed by intermediate rinsing with tap water and by acid cleaning with citric acid (2 hours immersion in 1.25 g L^{-1} in citric acid). The membranes were rinsed with tap water before they were replaced in the reactors.

4.2.2 Dead-end filtration cell setup

Several filtrations described in the following section were carried out in stainless steel stirred dead-end filtration cells, operated at different pressures, with different feed volumes and membranes. The comparability of the dead-end filtration cells to the spiral-wound module was given by the stirring of the feed to minimize concentration polarization on the membrane surface in the dead-end cell. For each test, a fresh membrane was cut, pre-wetted and the clean water flux was determined. The membrane area cut was 0.0044 m^2 and the total cell volume was 450 mL. The permeated volumes were weighed every minute by balances connected to a PC. Variables like applied feed solution, feed volume, membrane type and pressure were mentioned separately in each experimental section. Tests were performed in duplicate.

Total resistances were calculated from the flux, the pressure difference and the viscosity. The viscosity was assumed to be equal to that of water and was corrected for the temperature [10]. Rejections were calculated according to $1-(c_{permeate}/c_{feed})$.

4.3. Experimental approach

4.3.1 Nanofiltration

4.3.1.1 Dead-end nanofiltration tests for membrane selection

Dead-end filtration cells (section 4.2.2) were used at 4 bar on 450 mL mixed salt solutions (artificial MBR permeate) to select an appropriate NF membrane. Salt concentrations were in the range as in the MBR permeate of a separate continuous 60L lab scale MBR with identical membranes and settings (this reactor was not further used in this research). NF270 and NF245 (Dow), SR3 (Koch Membrane Systems, Inc.) and XN45 (TriSep) membranes were evaluated based on flux, (preferably high for high permeate water production for water reuse), low NaCl rejection and high phosphate rejection. A low NaCl rejection is important to prevent high salinity in the MBR tank, which might result in a deterioration of the biological performance. A high phosphate rejection is important when phosphate recovery from the NF concentrate is anticipated [2].

450 mL of a mixed salt solution was filtered, which was composed of NaCl, $CaCl_2 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$ and $Na_2HPO_4 \cdot 2H_2O$ (Boom BV, The Netherlands; VWR, The Netherlands) at concentrations of 300, 300, 716 and 150 mg L^{-1}, respectively. This resulted in total sodium, calcium, magnesium, chloride, phosphate sulphate concentrations of 159, 72, 66, 309, 81 and 273 mg L^{-1}, respectively. The permeate concentrations were determined after each test (see section 4.3.3) to calculate rejections. The tests were performed in duplicate. Table 4.2 summarizes the main characteristics of the tested membranes (as provided by the manufacturer).

Table 4.2. *Salt rejection and material characteristics of the four selected NF membranes (as provided by the manufacturer unless indicated differently).*

Membrane type	**NaCl rejection (%)**	**Clean water permeability (LMH bar^{-1})**	**Material**
Dow NF270	< 30 [11]	10.7	semi-aromatic piperazine based polyamide
Dow NF245	n.a.	8.6*	Fully aromatic polypiperazine amide
KOCH SR3	30-50	1.9	Proprietary TFC ® polyamide
Trisep XN45	25	4.9	Polyamide thin film composite

*this research; n.a. not available

4.3.1.2 Dead-end nanofiltration tests with MBR permeate

As no concentrate was produced from the R0% MBR permeate, the comparison of the performance over the NF was conducted in dead-end filtration cells. To compare the effect of R0% and R100% MBR permeate on NF fouling behavior, 450 mL of the permeates obtained at day 173 were filtered at 4 bar by the NF270 membrane in the dead-end filtration cells (section 4.2.2). Prior to filtration, the pH of each MBR permeate was adjusted from a pH around 7.8 to a pH of 8.0 using a 0.1 M NaOH solution.

In addition, the effect of pH (6, 7 and 8) on NF filtration behavior of R100% MBR permeate was evaluated. For each pH, 450 mL R100% MBR permeate was adjusted with 0.1 M NaOH or HCl, after which it was filtered over fresh samples of NF270 membrane material.

Finally, this procedure was repeated, with the difference that additional humic acids were added prior to pH adjustment. The TOC of the R100% MBR permeate was doubled from 15 to 30 mg L^{-1} using a humic acids stock solution containing 40 g L^{-1} of TOC (Humic acid sodium salt, Alfa Aesar, Germany).

Total filtration resistances in the three experiments were calculated as described in section 4.2.2.

4.3.1.3 Nanofiltration autopsies

Two NF autopsies were performed. The first one was performed on day 92 on the 2.5’’ NF270 module used in the MBR NF process, to get an impression of the occurrence and type of fouling/scaling on the NF membrane. For this the module was not cleaned after concentrate production as usually done, but the module was cut open. The fouling layer on a known NF membrane area was removed with a cell scraper and dissolved in ultrapure water. The composition of the solution was analyzed and from this the deposited amounts of organic and inorganic compounds (mg cm^{-2}) were calculated.

The second autopsy was performed on day 364 to compare and evaluate NF fouling potential of R0% and R100% MBR permeates. Dead-end filtration cells as described in section 4.2.2 were used, as no 2.5’’ NF module was present in the R0% reactor. 200 mL of both MBR permeates was collected, and each was filtered at 4 bar over a fresh NF270 membrane. As the entire MBR permeate volume should pass the NF membrane to be able to compare both layers and the fouling potential of both MBR permeates are not the same, only 200 mL (determined by pretests, data not shown) were used in the dead-end cell. The fouling layers deposited on the surface of the NF membranes were removed and analyzed as described above.

4.3.2 Membrane bioreactor

4.3.2.1 Critical flux step test

Critical flux step tests similar to the method described by Le Clech *et al.* [12] were carried out to compare the fouling behavior of the MBR membranes in both reactors. Regular membrane operation of both reactors was stopped at day 291, and all membranes were cleaned physically and chemically as described in section 4.2.1. After clean water flux measurement and reinstalling the cleaned membranes, the critical flux step experiments were performed with the reactors. The imposed flux of the Kubota plates was gradually increased from 7.5 till 25 LMH in steps of 2.5 LMH. Each flux level was maintained for 15 minutes before the next flux level was imposed. The pressure difference (dTMP/dt) between the end and the beginning of this 15 minutes at each flux step was calculated. An arbitrary dTMP/dt limit of 0.1 mbar min^{-1} [12] was used as a critical flux indicator. As fouling occurred, the actual flux may deviate slightly from the imposed flux. The flux values presented in the results section are the actual fluxes, calculated using the flows measured.

4.3.2.2 Dead-end filtration tests with MBR sludge

The contribution of different sludge fractions to MBR membrane fouling was investigated with stirred dead-end filtration cells. In each test a new Kubota membrane was used. All tests were conducted at 1 bar using 450 mL of sludge directly taken from the biological reactors, with 450 mL of the supernatants, and with the solids fraction of this sludge. Supernatant and solids fractions were produced by centrifugation (Alegra x-12R, Beckman Coulter Inc.) for one minute at 700 rpm. The solids were resuspended in 450 mL MBR permeate, sampled from the corresponding MBR. Filterability in all cases was expressed as total resistance (section 4.2.2).

4.3.3 Chemical analyses, SEM and saturation index

To determine the colloidal and dissolved chemical oxygen demand (COD) of the MBR sludge, samples firstly were filtered using a paper filtration (black ribbon filter, Wattman Grade 589) to remove suspended matter. Syringe filters with 0.45 µm pore size (VWR, The Netherlands) were subsequently used to remove colloidal matter and to obtain dissolved COD. Dissolved COD and COD after paper filtration were determined with test kits LCK 514, LCK 614 and LCK 314, (HACH LANGE GMBH), depending on the concentrations. After heat treatment in a thermostat (HT 200S, Hach Lange) at 170 ˚C, the concentrations of dissolved COD and COD after paper filtration were measured with a DR 3900 VIS spectral photometer (Hach Lange) at an automatically chosen wavelength in the range of 320-750 nm. Colloidal COD was calculated by subtracting the value for dissolved COD from the COD value after paper filtration.

Concentrations of anions, elements and organics were measured in 0.45 µm syringe filtered samples. Anions (chloride, phosphate and sulphate) were measured with ion chromatography (Compact IC 761, Metrohm). Elements (total sodium, calcium, magnesium, copper, potassium, phosphorous and sulphur amounts) were analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES; Optima 5300 DV, Perkin Elmer). Total carbon

(TC), inorganic carbon (IC) and total organic carbon (TOC) content were determined by a Multi N/C 3100 (Analytik Jena AG).

Samples of the fouled/scaled NF membrane were analyzed with a scanning electron microscope (SEM) JEOL-6480LV (JEOL Ltd., Tokyo, Japan) at 6 kV after the sample was dried for 24 hours. All samples were coated with a thin (10 nm) gold layer (JEOL JFC-1200 fine coater) before analysis under high vacuum.
Analytical software (Visual MINTEQ, Version 3.0, KTH, Department of Land and Water Resources Engineering) was used to analyze the saturation index in the MBR permeate streams. The saturation index equals the ion activity divided by the solubility product [13].

4.4. Results and discussion

4.4.1 Nanofiltration

4.4.1.1 NF membrane selection and rejections

As the rejection of the NF membrane determined to a large extent which components were recirculated to the MBR tank, proper selection of the NF membrane was essential. Selection of the NF membrane was based on ion rejections. Besides the mentioned low to intermediate NaCl rejection, a high phosphate rejection was preferred to enable phosphate recovery from the NF concentrate [2]. Figs. 4.2a and b summarize the results of the filtration experiments with the four pre-selected NF membranes. Based on these data, the type of NF membrane (2.5’’ module) for the integrated MBR NF system was selected.

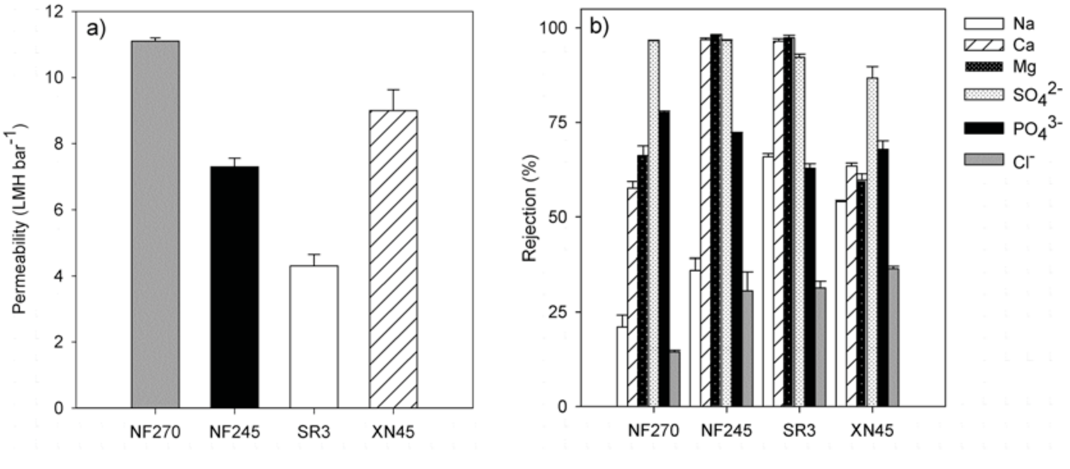

Fig. 4.2. *Rejection profiles a) and clean water permeabilities b) of NF270 and NF245 (DOW), SR3 (Koch Membrane Systems) and XN45 (Trisep) nanofiltration membranes for the mixed ion solution of NaCl, $CaCl_2$, $MgSO_4$, Na_2HPO_4 and $ZnSO_4$ as tested in dead-end cells in duplicate.*

The NF270 membrane had the highest permeability (11.1 LMH bar^{-1}) followed by the XN45 membrane (9.0 LMH·bar^{-1}) (Fig. 4.2a). A comparable clean water permeability of NF270 (12.3 LMH bar^{-1}) was found in literature [14], which is also in accordance with supplier data (Table 4.2). The other membranes gave slightly lower permeabilities than those provided by the supplier.

Desired performance was also reached by the NF270 membrane regarding the desired lowest sodium and chloride rejections (21 and 14%, respectively) (Fig. 4.2b). NF245 showed slightly lower values (36 and 31%, respectively). Also the calcium rejection was lowest for NF270 (58%), followed by XN45 (63%). Phosphate rejection was highest for NF270 with 78%, followed by NF245 (72%). Magnesium and sulphate rejections were slightly higher for the NF270 membrane (66 and 97%) and were lowest for XN45 (60 and 87%). Comparably low sodium and chloride rejections (below 10%), magnesium rejections of 50 to 55% and high phosphate rejections (90%) for the NF270 membrane at 4 bar were also found in literature [11, 14].

Overall, considering the desired requirements of low NaCl and high phosphate rejection combined with high flux, the NF270 is the most favorable membrane and therefore was selected for operation in the MBR NF system.

4.4.1.2 Influence of MBR permeate properties on NF performance

Table 4.3 gives an overview of the performance of the NF270 membrane in terms of ion concentrations in permeate and feed, and the corresponding ion rejections calculated from these. Results are shown for the 2.5’’ module operated with real wastewater in the continuous MBR NF setup as well as for the NF selection tests with synthetic MBR permeate.

Table 4.3. *Selected ion as well as inorganic carbon (IC) and total organic carbon (TOC) concentrations in NF feed (municipal MBR permeate) and NF permeate during concentration tests (concentration factor 4-6), and the corresponding rejections of the 2.5'' module in the integrated MBR NF system. For comparison, synthetic MBR permeate (NF feed) from the NF selection experiments and NF permeate concentrations as well as corresponding rejections are given (NF selection; see Fig. 4.2b).*

	setup	**Na**	**Ca**	**Mg**	**Cu**	**Cl^-**	**PO_4^{3-}**	**SO_4^{2-}**	**IC**	**TOC**
NF feed ($mg\ L^{-1}$)	MBR NF (R100%)	149 ± 24	85 ± 9	25 ± 5	0.52 ± 0.25	192 ± 54	18 ± 4	43 ± 25	51 ± 11	17 ± 4
NF permeate ($mg\ L^{-1}$)		103 ± 30	37 ± 9	4.5 ± 2.5	0.11 ± 0.05	123 ± 44	0.2 ± 0.1	0.6 ± 0.2	22 ± 6	0.5 ± 0.44
NF rejection (%)		31	57	78	79	36	99	99	58	97
NF feed ($mg\ L^{-1}$)	Dead-end	159	72	66	n.a.	309	81	273	n.a.	n.a.
NF permeate ($mg\ L^{-1}$)		126 ± 4.9	31 ± 1.3	22 ± 1.7	n.a.	265 ± 1.5	18 ± 0.3	9 ± 0.3	n.a.	n.a.
NF rejection (%)		21 ± 3.1	58 ± 1.8	66 ± 2.6	n.a.	14 ± 0.5	78 ± 0.3	97 ± 0.1	n.a.	n.a.

Although the NF performance is an important parameter, also other factors like wastewater quality or biological and membrane MBR performance influenced the actual NF rejection and fouling behavior. The composition of the two feed solutions in Table 4.3 was similar for sodium and calcium, whereas magnesium, chloride, phosphate and sulphate were higher in the synthetic feed than in real MBR permeate. Comparing rejections of the MBR NF system to those of the dead-end filtration tests, rejections for sodium, magnesium, chloride and phosphate of the NF module in the MBR NF system were higher than the ones obtained in the dead-end filtration. The higher rejections may be related to the higher feed pressure (11 bar) in the MBR NF system compared to that in the stirred dead-end filtration cell (4 bar) [15] or due to the lower feed concentrations.

Additionally, as scaling in the 2.5'' module could not be identified separately, it most likely added up to the overall rejection. Calcium and sulphate rejections were comparable in both cases. In the MBR NF system, rejections for total inorganic and organic carbon were found to be as high as 58 and 97%, respectively. High rejection of organic carbon could increase the ion rejections due to adsorption of some of the ions on the organic molecules, which subsequently got rejected together with the organic carbon [16]. Generally this phenomenon is very dependent on the feed water composition.

The phenomenon mentioned may play an important role regarding the effect of copper on the biological activity of the MBR system. Copper rejection of the NF was 79%. Increased concentrations of copper in the MBR feed due to the nanofiltration recirculation might be potentially toxic to microorganisms. Copper concentrations of 0.02 mg L^{-1} already led to 22% inhibition (decrease in specific oxygen uptake rates), while 0.9 mg L^{-1} even led to 91% inhibition [17]. However, the effect of increased copper concentration on MBR performance might be very dependent on the sludge matrix as other research showed that 0.5 mg L^{-1} already caused 82% inhibition [18].

The recirculated NF concentrate in the R100% MBR reactor potentially lowered the NF rejections due to the higher load onto the NF membrane during the concentration test. More details on NF scaling are given in section 4.4.1.4. Nevertheless, the NF permeate quality remained very good with rather low concentrations of inorganics, also compared to the artificial permeate (Table 4.3). The NF permeate of the R100% MBR can be classified as suitable for water reuse for several industrial processes or even for direct potable reuse [19].

4.4.1.3 Fouling potential of MBR permeate on the NF membrane

It can be expected that recirculation of recalcitrant organic compounds such as humic acids and inorganic species changed the composition of MBR permeate, and thus effected the NF fouling behavior. Dead-end filtration tests with each MBR permeate at pH 8 confirmed this (Fig. 4.3).

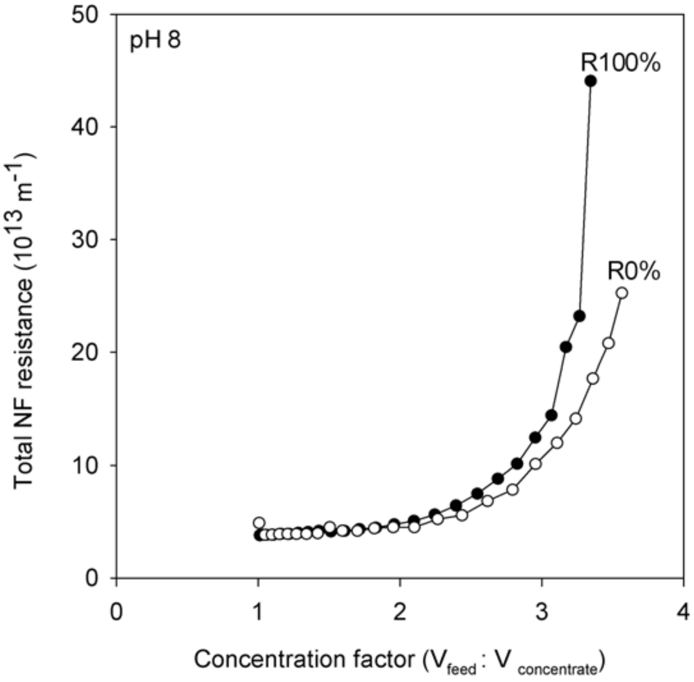

Fig. 4.3. *Total NF resistance as a function of the concentration factor inside the dead-end filtration cell. R0% and R100% MBR permeate at pH 8.*

The resistance of the R100% MBR permeate started to increase earlier than that of the R0% MBR permeate. This may have been caused by higher concentrations of divalent cations (e.g. calcium) in R100% MBR permeate compared to those in R0% MBR permeate. However, concentrate recirculation can also result in higher concentrations of (recalcitrant) organic compounds in the MBR permeates (TOC of R100%: 18.1 ± 7.5 mg L^{-1}; R0%: 12.7 ± 6.2 mg L^{-1}). The Ca^{2+}/TOC ratio of R100% MBR permeate was 4.8, compared to a value of 5.3 for R0% MBR permeate. This shows that in comparison more inorganics were available for NF fouling due to the much higher TOC rejection in the MBR than calcium. Therefore, scaling was expected to occur primarily, nevertheless both foulants are likely to interact and determine the overall fouling behavior, which needs to be elucidated in more detail to evaluate the fouling process.

It is known that the interaction between organics and inorganics depends on the pH [20, 21]. Not only the occurrence of scaling and organic fouling changes with pH, but also the surface charge (degree of protonation) of the negatively charged NF270 membrane. The NF270 has an isoelectric point of 3.2 [22] and is therefore deprotonated at neutral pH. To investigate this further, the dependency of the NF resistance on feed pH was investigated using the R100% MBR permeate because of its faster increase in resistance at pH 8 (Fig. 4.3). The results are shown in Fig. 4.4.

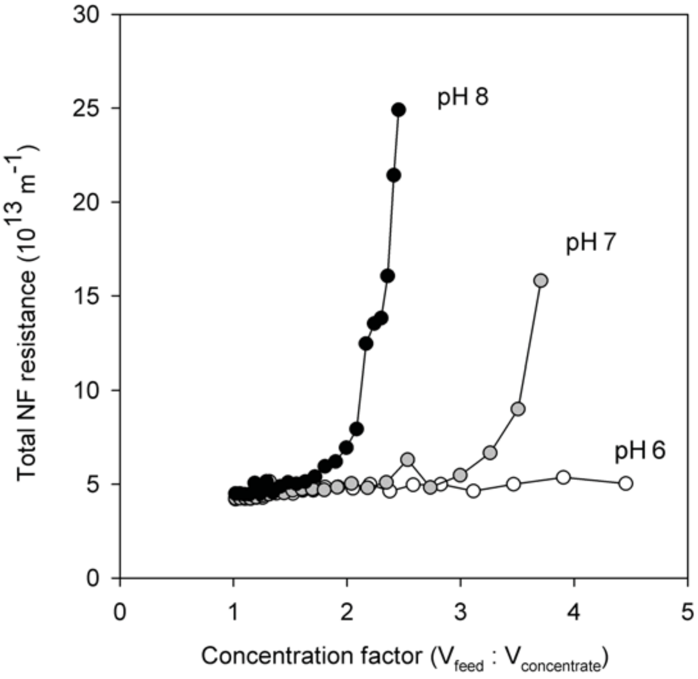

Fig. 4.4. *Total NF resistance as a function of the concentration factor of the MBR permeate (R100%) at pH 6, 7 and 8.*

Filtration of the R100% MBR permeate samples at different pH values showed that the resistance increased with increasing pH (Fig. 4.4). At pH 6 no influence on the resistance was measurable due to the low impact of the scaling, as will be explained later. This is not in agreement with literature [20, 21] where the filtration of humic acids in solution with 10 mM NaCl led to flux a decline at lower pH, possibly due to adsorption of the humic acids on the membrane surface at a low pH. At higher pH the degree of dissociation of the functional groups, i.e. carboxylic acid or phenolic groups, of the humic acids as well as the membrane surface increased [23], resulting in a more negative charge of the humic acids as well as of the membrane surface. This led to increased electrostatic repulsion between the membrane and the organic compounds at higher pH and consequently less fouling [20]. However, this was done in artificial solutions with humic acids and not with real MBR permeate containing more components than just humics.

In the case of more realistic MBR permeate from municipal wastewater, it is important to also take the interaction of humic acids and inorganics (cations), i.e. calcium, into consideration. Literature reports that the presence of calcium in combination with humic acids in artificial solutions increases fouling [20] due to the interaction between calcium and the negatively charged groups of the humic acids. This decreases the electrostatic repulsion between humic acids and the membrane surface, which promotes flux decline. Fouling by humic acids in the presence of calcium is known to be worse at lower pH than at higher pH [20]. Since our results showed that fouling increased at higher pH, organics may not have been the main contributor to the increased filtration resistance observed in Fig. 4.3. To verify this, additional organic carbon (humic acids) was added to the feed and the resistance at different pH values was monitored again (Fig. 4.5).

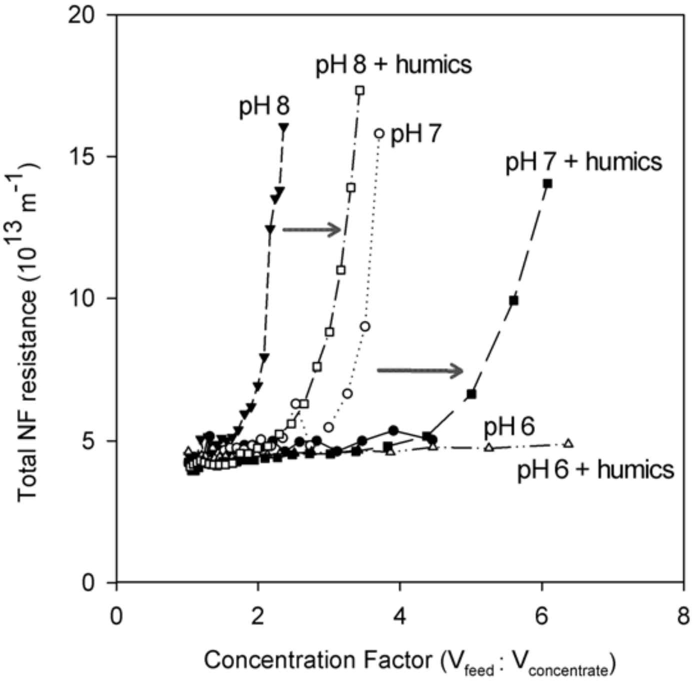

Fig. 4.5. *Fouling behavior of the MBR permeate (R100%) at different pH (6, 7 and 8) after addition of additional organic carbon in the form of humic acids.*

At pH 6 no resistance increase was measurable without or with additional organic carbon over the applied concentration factor range. Again this can be related to the minor impact of the inorganics at lower pH as described later. Surprisingly, for pH values of 7 and 8, doubling the TOC value caused a delay in the resistance increase. It is possible that the increase in TOC concentration increased the electrostatic repulsion between the organics and the membrane (especially at a higher pH), thereby decreasing the bridging between the organics and the membrane surface, which finally leads to less fouling. This result supported the hypothesis that organics were not the major cause of fouling in this case, but apparently the inorganics. Additionally, the large contribution of inorganic fouling to the flux decline of the NF was supported by the fact that the most efficient cleaning method to restore the flux of the 2.5’’ module was the use of citric acid at pH 4. The use of alkaline cleaners did not restore or improve the flux (data not shown). Also in literature citric acid was also found to be very efficient for inorganic scaling [7].

This is an important finding and is supported by the data obtained at the beginning of the continuous experiment compared to those obtained at the end of the experiment. These show that the overall Ca^{2+}/TOC ratio in the NF concentrate (pH 8) dropped from 4.2 (130 mg Ca^{2+} L^{-1}/ 31 mg TOC L^{-1}) at the start to 2.7 (144 mg Ca^{2+} L^{-1} / 53 mg TOC L^{-1}) at the end of the experimental period. This can be explained by the higher TOC rejection (97%) by the NF compared to that of calcium (57%) in the R100% system (Table 4.3). With decreasing Ca^{2+}/TOC ratio also the relative impact of the organic fouling can increase in time, and become more pronounced while inorganic precipitation may become relatively less important. Based on calculations of the saturation potential of the MBR permeate (using the MINTEQ software), most likely calcium phosphate precipitation as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) on the membrane surface occurred (saturation index above 10). The faster flux decline at higher pH can then be explained by an increased availability of orthophosphates (PO_4^{3-}) due to a shift from HPO_4^{2-} to PO_4^{3-} at a higher pH. It would also explain why the impact of the calcium phosphate at pH 6 is less significant (Fig. 4.4 and 4.5), where more than 90% of the phosphate species are present as $H_2PO_4^-$ and the saturation index for hydroxyapatite was ten times lower, at around 1.8. This confirms our hypothesis that fouling on the NF membrane was predominantly caused by precipitation of calcium phosphate.

The presented filtration tests at different pH values gave rejections for calcium at pH 6, 7 and 8 of 21%, 25% and 38%, respectively. At similar calcium concentrations in the feed in all dead-end tests, the addition of humic acids in these filtration tests increased calcium rejections to 27%, 35% and 43%, respectively. This increase can be attributed to the interaction of calcium and humic acids, as mentioned earlier. With and without additional organic carbon, increasing rejections with increasing pH can be explained by the increased deprotonation of the organics as well as of the membrane surface at increased pH. Also the precipitation of calcium phosphates could have added up to the overall rejection, as this is more favorable at higher pH.

Conclusively, the difference in rejections between R0% and R100% MBR permeate, the delayed resistance increase in the presence of additional organics and the decrease in the ratio of calcium to TOC towards the end of the MBR NF experimental period for R100% all indicate that higher organic carbon concentrations in an integrated MBR NF process with concentrate recycle lowered the impact of inorganic compounds on NF fouling during operation.

Another issue is that the recirculation of concentrate caused an increase in heavy metal load to the R100% reactor due to the high copper rejection of the NF membrane (79%). A typical copper load was 17.2 ± 7.4 mg day^{-1} for the R100% MBR system, compared to 12.6 ± 8.2 mg day^{-1} for the MBR without recirculation. This increased copper load may cause stress to the microorganisms in the MBR. However, this is accompanied by higher concentrations of organics, that can bind copper and in this manner may alleviate this stress [24].

4.4.1.4 Nanofiltration autopsies

In an early stage, i.e. after 92 days of operation, an NF autopsy of the 2.5’’ NF270 module used for concentrate production for the R100% MBR was performed to determine the nature of the deposition. A representative area of deposited material on the surface of the membrane was scraped off from the membrane and its composition was analyzed for elements and organics (Fig. 4.6).

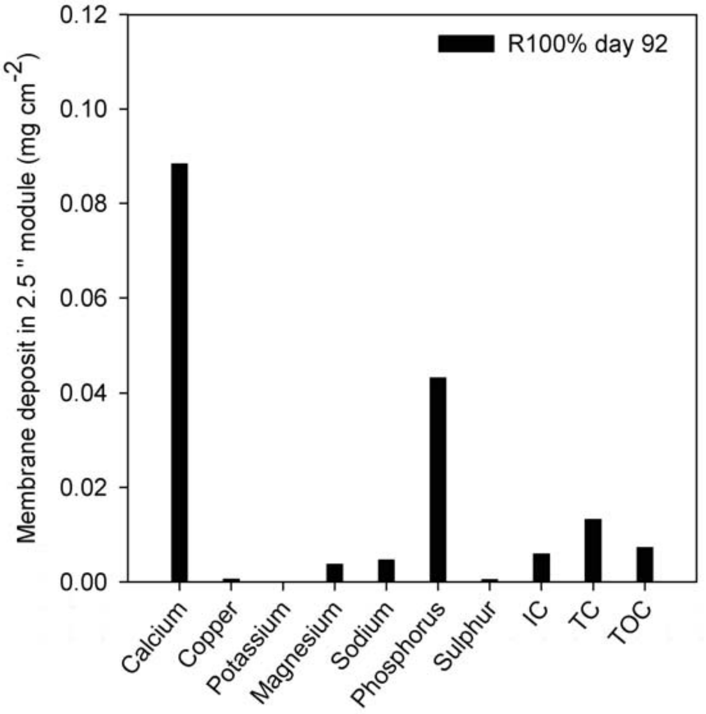

Fig. 4.6. *Composition of the deposit on the NF from the 2.5’’ NF module autopsy at day 92 after concentrate production for R100% without cleaning.*

Fig. 4.6 clearly shows that calcium and phosphorous were the main elements on the membrane surface. Compared to those, elements like copper, potassium, magnesium, sodium, and sulphur as well as organic carbon were found in relatively low amounts. Simulations on the scaling potential of the NF feed using analytical MINTEQ simulation software confirmed that the R100% MBR permeate had a clear potential for hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) precipitation already at this stage of the operation with a saturation index of 11.2.

A second autopsy was done at day 364 to investigate the effect of concentrate recirculation on the performance of the NF membrane and long-term deposition. Also here, analytical MINTEQ simulations showed a saturation index for hydroxyapatite for the R100% MBR of 11.7. This was slightly increased, not only compared to that on day 92, but also compared to the R0% MBR at day 364 (saturation index: 10.2). Calcium phosphate scaling remained a significant issue over the entire experimental period. This also explains the results of the filtration tests (Figs. 4.4 and 4.5). For the second autopsy, 200 mL of each MBR permeate (R0% and R100% at day 364) were filtered over fresh NF270 membrane material in stirred dead-end filtration cells. The deposit composition was compared for both samples (Fig. 4.7).

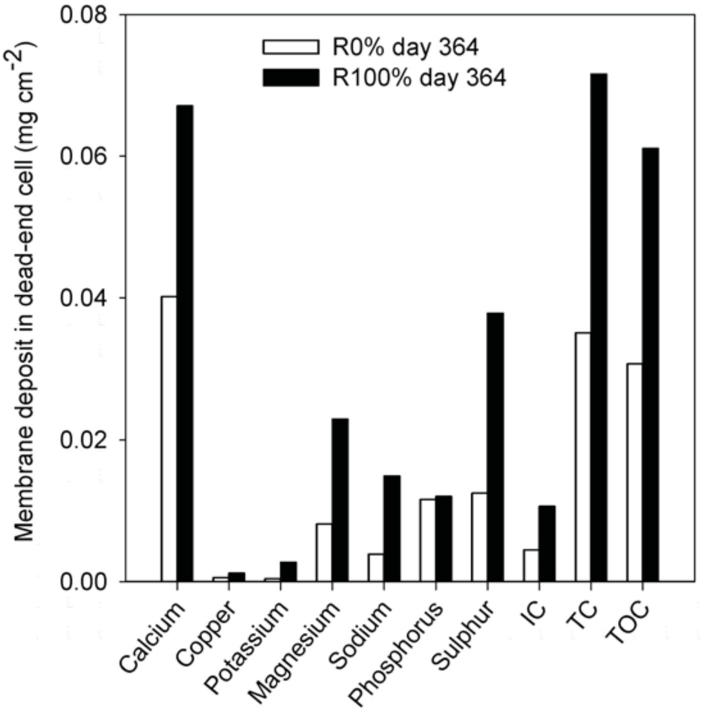

Fig. 4.7. *Composition of the deposited layer on the NF270 membrane after filtration of the R0% and R100% MBR permeate of day 364 in the stirred dead-end filtration cells.*

In this later stage, filtration of the 200 mL R0% MBR permeate caused less deposition on the NF membrane than filtration of 200 mL R100% MBR permeate. In both reactors calcium, magnesium, sulphur and total organic carbon were predominantly present. Phosphorous however showed rather similar values. This could only be explained by the fact that calcium phosphate precipitation in the MBR tank was observed, which led to a lower concentration factor of phosphorous. An indication for this are for example the concentrations of species in the two MBR permeates at the end of the experimental period. Sulphur concentrations in the R100% MBR permeate were 1.8 times higher than in R0%. However, phosphorous concentration was only 1.3 times higher in R100% compared to R0%. With the same NF rejection of 99% (Table 4.3) the sulphur and phosphorous concentrations should have been rather equal unless precipitation of these components occurred. As calcium phosphates were saturated, it is also likely that those already formed precipitation in the liquid as the concentration factor slightly increased.

Although an exact quantitative comparison of the different experiments at day 92 and day 364 was not possible (different filtered volumes), the autopsies show that in both cases the calcium content was high. This was possibly due to the high calcium concentrations in the wastewater (67 ± 10 mg L^{-1}) compared to magnesium, sodium or potassium, and the high rejection by the NF membrane (calcium: 57%)(Table 4.3).

High calcium concentrations are also in agreement with the calcium phosphate scaling observed during the first autopsy in the R100% system, which still seems to be present at the final stage according to the analytical calculations. However, calcium phosphate precipitation was accompanied by sulphur, magnesium and sodium scaling, and also by high amounts of organics. This additionally explains why the phosphorous content on the membrane surface was lower in the later stage, as the calcium phosphate precipitate may have been accompanied by that of other counterions (e.g. sulphate). However, no sulfur containing precipitations were suggested by the MINTEQ calculations, but these calculations are very rough estimates based on ions in pure water.

TOC concentration in the R100% MBR permeate was higher compared to that in the R0% MBR permeate, possibly due to recirculation of TOC in the NF retentate (TOC rejection 97%, Table 4.3) back to the R100% reactor. The autopsy data further showed that the Ca^{2+}/TOC ratio in the deposit on the membrane decreased from 9 (day 92) to a value of 1 (day 364), due to increased amounts of organics (day 92: 0.007 mg TOC cm^{-2}; day 364: 0.061 mg TOC cm^{-2}) and a slightly lower amounts of calcium (day 92: 0.088 mg Ca^{2+} cm^{-2}; day 364: 0.067 mg Ca^{2+} cm^{-2}) at the end of the experiment (Fig. 4.6 and 4.7).

Additionally, SEM-EDX was carried out to confirm the fouling on the membrane surface after the dead-end filtration tests. Quantitative data are presented in Table 4.4.

Table 4.4. *Relative atom percentages of main contributing elements determined with SEM-EDX in the MBR permeate at day 364 for R0% and R100%.*

		rel. atom %	
		R0%	R100%
C		28.03	46.57
O		56.12	44.44
	sum	84.15	91.01
Mg		0.78	0.44
P		4.62	2.72
Ca		10.45	5.83
	sum	15.85	8.99

This shows that the sum of the relative amounts of inorganics (magnesium, phosphorous, and calcium) in the R100% recirculation reactor was higher (15.85%) than in the R0% reactor (8.99%). This was due to the relatively higher amount of organics (sum of C and O: 91.01%) in the deposition layer on the membrane surface of R100% compared to the blank (sum of C and O: 84.15%). This can be directly related to the MBR permeates in this final stage: the concentration of organic carbon in the R100% system was nearly twice as high as in the R0% permeate, while the calcium concentration only was 23% higher compared to R0% permeate. This confirms the trend in the autopsies, where relatively higher organic concentrations were found in the R100% system.

Concluding, it is observed that the NF operation was highly impacted by calcium phosphate scaling (later accompanied by other inorganic compounds as well as some organics), especially at higher pH.

4.4.2. MBR

For all four MBR Kubota membranes (2 membranes per reactor), the TMP was recorded in time. The results clearly demonstrated (full data set not presented here) that the R100% system with recirculation exhibited a faster increase of the TMP and a higher absolute TMP value during the entire experimental period. Fig. 4.8 gives a representative example of one hour for each pattern of the TMP data.

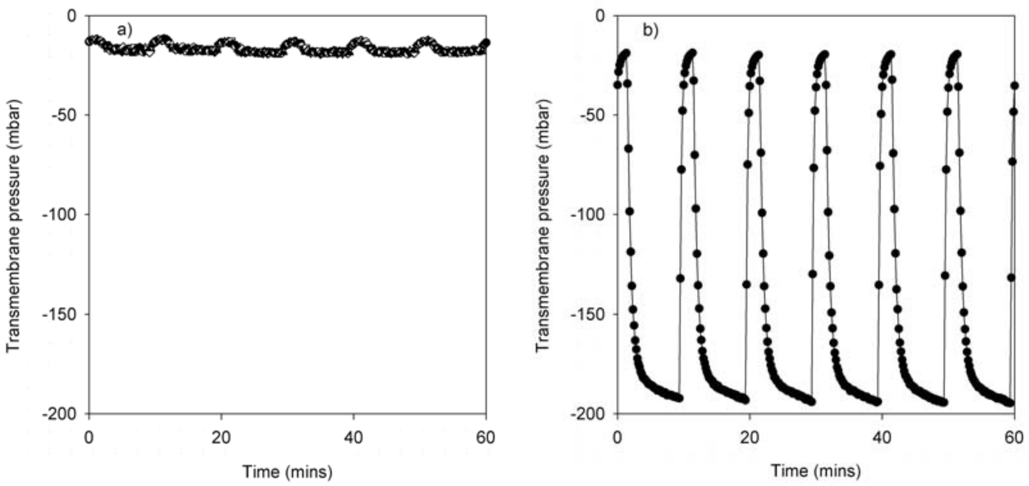

Fig. 4.8. *Representative TMP profiles of one hour during continuous MBR operation for a) the R0% (no recycle) and b) R100% (full recycle) MBR.*

The R100% MBR showed continuously increasing TMP values (Fig. 4.8b), requiring frequent cleaning. The TMP of the R0% MBR nevertheless (Fig. 4.8a) hardly increased during filtration and remained below -100 mbar. This was mainly the consequence of the cleaning strategy, according to which the two stronger fouling R100% membranes determined the cleaning frequency of all four membranes. This also implied that the two membranes in the R0% MBR operated below their critical flux.

During cleaning of the membranes it was clearly visible that the membranes in R100% were covered with a dense gel-type layer, whereas the membranes in the R0% MBR were covered with a much more open layer, easier to remove by physical cleaning than the layer of R100%. This suggested that the membranes in the R100% MBR were operated above their critical flux. To verify this hypothesis, critical flux measurements for both reactors were carried out [12]. The pressure difference over time (dTMP/dt) at the start and end of each flux step was determined, and plotted as a function of the flux (Fig. 4.9).

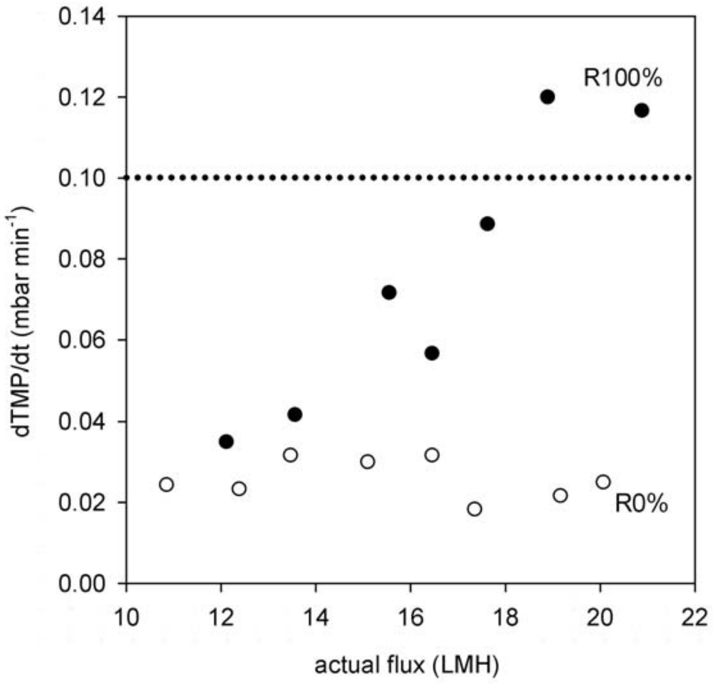

Fig. 4.9. *Pressure difference (dTMP/dt) over time during 15 minutes flux steps as function of the actual operational flux (LMH) for the MBR without NF concentrate recycle (R0%) and the system with full recycle (R100%). Dashed line: arbitrarily defined dTMP/dt limit used as critical flux indicator [12].*

Fig. 4.9 shows that the dTMP/dt of the R0% MBR did not significantly change (0.02 to 0.03 mbar min^{-1}) over the entire imposed flux range. Apparently the critical flux for this reactor was higher than the maximum imposed flux of 25 LMH. For the R100% MBR the dTMP/dt started to increase already at the lower fluxes, indicating that recirculation of NF concentrate drastically reduced the critical flux in comparison. The critical flux of the R100% MBR was located between 18-20 LMH, using the threshold value of 0.1 mbar min^{-1}. Both reactors were operated at 7.5 LMH during the continuous operation over 364 days, well below the critical flux calculated from Fig. 4.9. The two weekly cleaning frequency, only determined by the R100% MBR, indicated that the threshold value of 0.1 mbar min^{-1} [12] is too high for our MBR NF recirculation system even though the reactors were run with a continuous relaxation step. The faster TMP increase for R100% may have been caused by higher concentrations of dissolved and colloidal organic matter [25] such as humic acids or free EPS.

To investigate the fouling potential of the sludge, and the solids and supernatant fractions of these sludges, filterability tests were performed with samples from both reactors. Total sludge mixture (supernatant and solids), supernatant, and solids (with the supernatant replaced by

MBR permeate) were filtered separately over Kubota membranes in dead-end filtration cells (Fig. 4.10).

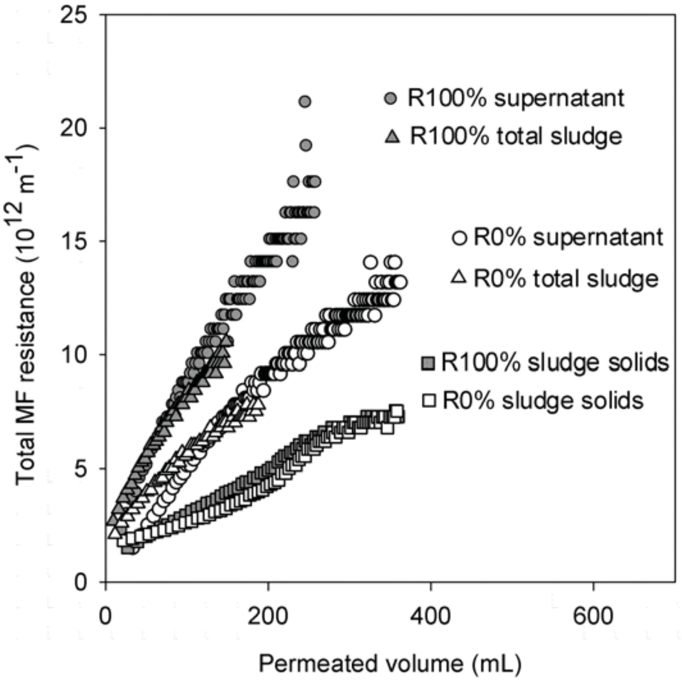

Fig. 4.10. *Comparison of fouling potential of total sludge, sludge solids and supernatant of the R0% and R100% MBR, expressed as the total filtration resistance versus the permeated volume.*

Fig. 4.10 shows that the total MF resistance of the sludge mixture is higher for the R100% MBR than for the reactor without recycle (R0%). This is in line with the higher TMP data observed for the R100% MBR (Fig. 4.8b) and with the critical flux data (Fig. 4.9). The data in Fig. 4.10 confirm the hypothesis that the total resistance of the sludge mixture is specifically caused by the supernatant fraction in both reactors. A similar behavior was found for the sludge quality and filterability during the start-up of a full scale MBR plant in Varsseveld, The Netherlands [26]. In our case, the sludge solids (mixed with permeate) gave a lower resistance than the supernatant and the total sludge mixture and therefore seemed to have contributed to less to the overall fouling. In addition, MF resistances caused by the solids were similar for the two reactors. From the above it can be concluded that recirculation of NF concentrate elevated the fouling potential in the MBR, and that fouling was mainly caused by the supernatant of both reactors. An analysis of both MBR supernatants in terms of COD fractions was performed, and the results are shown in Fig. 4.11.

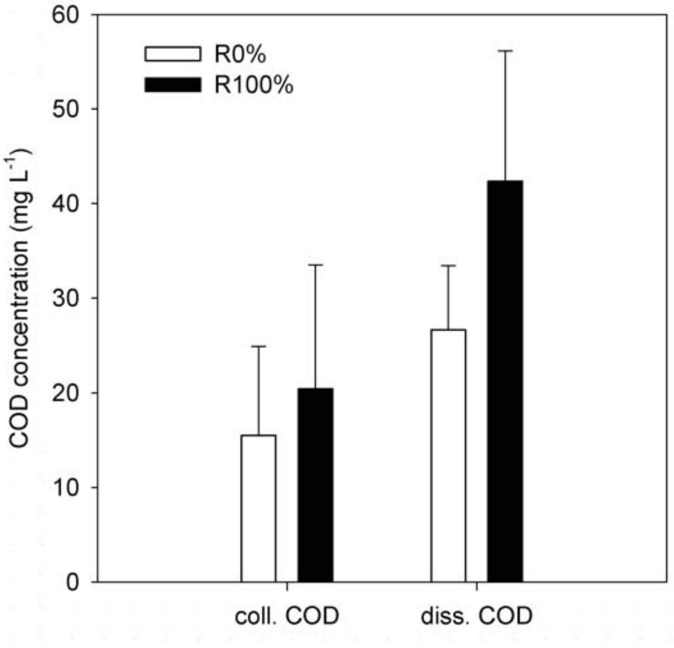

Fig. 4.11. *Average concentration of colloidal and dissolved COD in the supernatant of the R0% and R100% MBR over 364 days.*

Although the values showed considerable variations over time (data not shown over time), dissolved and colloidal COD were always higher in the R100% MBR supernatant than in the R0% MBR supernatant. The increased dissolved COD for R100% probably was directly related to the NF concentrate recirculation. The colloidal COD could be related to changes in the floc structure, but may also have resulted from EPS or humics. Tighter flocs, due to the bonding of EPS and divalent ions, might not have been able to capture enough colloidal material, which therefore might have promoted fouling. It cannot entirely be pointed out which fraction, colloidal or dissolved, was the main contributor to the MBR fouling.

To summarize, this work shows that the operation over one year of an MBR NF process under full recirculation conditions is feasible. The NF permeate quality was not impacted significantly by the recirculation, and therefore this concept creates a valuable source for water reuse from wastewater. However, this research also demonstrated that especially dissolved and colloidal COD present in the supernatant of the MBR influenced the MBR membrane performance significantly. The MBR supernatant composition therefore can be directly related to the fouling behavior of the MBR membranes. Since it cannot be pointed out which fraction was the main reason for fouling, intermediate NF concentrate treatment for the removal of dissolved COD as suggested in literature (oxidation or adsorption [4]), may be necessary to lower the fouling. Additionally, the recovery of valuable calcium phosphates from the NF concentrates before its recirculation to the MBR could be beneficial for the flux decline caused by inorganic calcium phosphate scaling in the NF operation. This would not only enhance the NF operation but also lower the scaling potential in the MBR tank.

For future research it is suggested that the selection of different types of membrane material or even the use of other module configurations might help to encounter fouling problems in the MBR. For instance, a side stream MBR would improve the cleaning procedure. Submerged capillaries could also be applied, which would make backwashing possible.

Finally, the impact of NF concentrate recirculation and increased inorganic content in the sludge on downstream sludge processing, e.g. the sludge dewatering, is unknown. More research in this regard needs to be performed.

4.5. Conclusions

The experimental results of the long-term operation (1 year) presented show that the continuous production of reusable water from wastewater in a combined MBR NF process with NF concentrate recirculation is very well feasible.

The NF permeate quality is not impacted by the recirculation. Fouling on the NF membrane is mostly the result of inorganics, while organics (e.g. humic acids) do not have a major impact on the fouling. In fact, the flux of the NF was enhanced by the presence of humic acids due to the recirculation, which indicates that the ratio of organics to inorganics positively can impact the system performance. Regarding the MBR performance, the results show increased fouling due to the NF concentrate recirculation. TMP and critical flux increase and consequently more frequent MBR membrane cleaning is required for the system with recirculation.

Acknowledgements

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List of abbreviations

COD	Chemical oxygen demand
EPS	Extracellular polymeric substances
HRT	Hydraulic retention time
IC	Inorganic carbon
LMH	L m^{-2} h^{-1}
MBR	Membrane bioreactor
MF	Microfiltration
NF	Nanofiltration
PBS	Phosphate buffer saline
RO	Reverse osmosis
SEM	Scanning electron microscope
SRT	Sludge retention time
TC	Total carbon
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration

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5

Electrochemical phosphate recovery from nanofiltration concentrates

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Abstract

The high total phosphorus content of raw domestic wastewater with its significant eutrophication potential offers an excellent possibility for phosphate recovery. Continuous recirculation of NF concentrate to an MBR and simultaneous phosphate recovery from the NF concentrate can be applied to produce reusable water, recovering phosphates, while at the same time decreasing the scaling potential of the recirculated NF concentrate, prolonging the retention times of slowly biodegradable soluble compounds (e.g. micropollutants) and recirculating multivalent cations to promote the bio-flocculation. Here we introduce an electrochemical system to recover phosphates. An electrochemical cell was divided into an anode and a cathode compartment separated by a cation exchange membrane. Precipitation of phosphates from nanofiltration concentrate was induced by locally increasing the pH at the cathode surface by water electrolysis and thereby creating supersaturated conditions at the cathode. 80 to 95% recovery of total phosphate was achieved at a pH of 8 to 10 near the cathode. Ion analysis, XRD and ATR-FTIR spectra indicated that the precipitate consisted of amorphous calcium phosphate (ACP) and minor proportions of amorphous calcium carbonate (ACC). The amount of ACC was dependent on the pH. Calcium phosphate scaling at the cathode surface did not occur due to H_2-gas formation preventing nucleation and growth at the cathode.

5.1. Introduction

Recovery of phosphates and production of reusable water present new challenges in domestic wastewater treatment and are important elements in balancing human utilization of planetary resources [1]. Due to the large volumes of domestic wastewater produced, the phosphate load in this water is high, even though the concentrations are relatively low (4-16 mg PO_4^{3-}-P L^{-1}) [2]. Phosphate has a large eutrophication potential, therefore it needs to be removed before the water can be discharged. Generally this is accomplished by chemical precipitation with metal salts, or by enhanced biological phosphorus removal. In both cases the phosphorus ends up in the excess sludge line and finally will be wasted.

Due to the high value of phosphates as a resource, a much better option would be to recover and reuse phosphates from domestic wastewater [3]. Phosphate recovery from the water line is possible, for example by crystallization [4], but because of the low concentrations this is not very effective. Nowadays, membrane concentrates evolving from wastewater treatment are a potential source for phosphate recovery as well. A membrane bioreactor (MBR) followed by a nanofiltration membrane (NF) can be applied to produce reusable water. The NF permeate can be used for e.g. households, industrial processes or as irrigation water [5, 6]. NF concentrate disposal to surface waters or landfills however, has serious environmental impacts and remains the bottleneck of this application [7]. To address this issue, continuous recirculation of NF concentrate to an MBR and simultaneous phosphate recovery from the NF concentrate can be applied in an integrated process to recover the phosphorus, while at the same time decreasing the scaling potential of the recirculated NF concentrate on the NF membranes [8], prolonging the retention times of slowly biodegradable soluble compounds (e.g. micropollutants) [9], and recirculating multivalent cations to promote the bio-flocculation, which may reduce fouling of the MBR membranes [10].

Caustic soda can be added to create supersaturated conditions at high pH to induce crystallization of phosphorus as calcium phosphates [11]. Phosphate precipitation, for instance as amorphous calcium phosphate (ACP), monetite, brushite or hydroxyapatite (HAP), is dependent on the conditions available for supersaturation, i.e. chemical equilibria and thermodynamic solubility products (Table 5.1) [12, 13] but is also strongly kinetically determined.

Table 5.1 *Overview of most common calcium phosphates with respective molar calcium to phosphate ratios [12, 13].*

Compound	Reaction equation	Ca/P ratio
Brushite	$HPO_4^{2-} + Ca^{2+} + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O$	1.0
Monetite	$HPO_4^{2-} + Ca^{2+} \rightarrow CaHPO_4$	1.0
Octacalcium phosphate (OCP)	$8Ca^{2+} + 6HPO_4^{2-} + 5H_2O \rightarrow Ca_8H_2(PO_4)_6 \cdot 5H_2O + 4H^+$	1.3
ACP	$2HPO_4^{2-} + 3Ca^{2+} + 3H_2O \rightarrow Ca_3(PO_4)_2 \cdot 3H_2O + 2H^+$	1.5
Hydroxyapatite	$3HPO_4^{2-} + 5Ca^{2+} + 4OH^- \rightarrow Ca_5(PO_4)_3OH$	1.7

Caustic soda addition to create alkaline conditions, as used in technologies like the Crystallactor® process or the Kurita fixed bed crystallization column [14], can be avoided by using water electrolysis. Electrochemical precipitation has been used for water softening [15] to remove carbonate hardness from cooling water systems in order to prevent scaling. Commonly, both electrodes are simultaneously present in the treated solution. More recently, a system to remove phosphates from MBR feed using the aluminum of the electrodes to precipitate solid aluminum phosphate through coagulation has been described [16]. However, in that case, the desired reactions with electrode material resulted in undesired replacement costs. Another electrochemical system, where both electrodes were in the same solution to precipitate struvite from artificial electrolytes at neutral pH was described [17]. However, the deposition of precipitates at the electrode surface decreased the efficiency. Finally, an electrochemical application for calcium carbonate hardness reduction in cooling waters including an ion exchange membrane to separate the cathode and anode compartment was introduced [18]. This process could also be used for phosphate recovery. Starting from these electrochemical processes, we propose an integrated concept that combines domestic wastewater treatment in an MBR NF system (including continuous NF concentrate recirculation to the MBR) with an electrochemical process to recover phosphate. Compared to other techniques to recover phosphate, it has the advantage that salts and base are not required and no transportation of chemicals and replacement costs for electrode material are needed.

In this research we provide a proof of principle of a batch EPR concept for electrochemical phosphate recovery using real MBR NF nanofiltration concentrate as feed for the EPR. In this first study, the performance of the cathode process is evaluated and compared with the recovery obtainable with e.g. those of the commercially available Crystallactor® process.

Based on an average of 5 mg PO_4^{3-}-P L^{-1} in the wastewater inflow, an NF rejection for phosphate of 85% and an NF water recovery of 80%, the P concentration in the NF concentrate is 22 mg L^{-1}. With an assumed phosphate recovery by the EPR of 80%, a phosphate recovery of 70% of the wastewater inflow is calculated. This would be comparable to the P-recovery obtainable with the commercial Crystallactor®, which is between 65-70% [19].

To the best of our knowledge this is the first time such a study on an enhanced phosphate recovery (EPR) system including a cation exchange membrane has been conducted on MBR NF concentrates from real domestic wastewater coming from a NF concentrate recirculation loop.

5.2. Principle EPR

Fig. 5.1 shows the principle of the batch EPR process for the recovery of phosphates from NF concentrate. This batch process is used here to prove that phosphate recovery from NF concentrates is indeed possible. In this case both anode and cathode compartment are fed separately with the same NF concentrate. In a continuous process however, the NF concentrate could first pass the anode (low pH) to strip the carbonates and then pass the cathode compartment to recover phosphate (high pH).

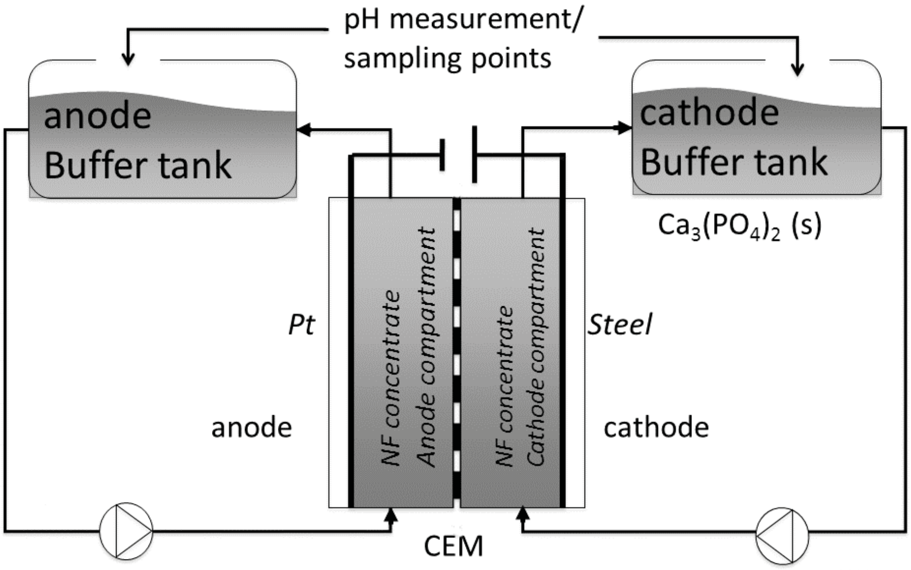

Fig. 5.1. *Schematic view of the non-continuous electrochemical setup for the recovery of phosphates; including electrochemical cell, electrodes, CEM, buffer tanks, pumps and power supply.*

The anode and cathode are separated by a cation exchange membrane (CEM). This membrane separates the electrolytes with low (anode) and high (cathode) pH, and allows the control of the pH in both chambers without neutralization of the solutions, thus dramatically increasing the process efficiency due to the much higher pH obtainable in the cathode and required for efficient phosphate recovery. At the anode and the cathode, the following reactions occur:

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Cathode: $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$

At a pH range of the NF concentrate of 7-7.8, potential crystallization of calcium phosphates is limited; especially in wastewaters that contain humic acids, formation of such crystals can be inhibited [20]. The production of OH^- ions in the cathode chamber increases the pH in that compartment, causing $H_2PO_4^-$ ions to convert mainly to HPO_4^{2-} and/or to PO_4^{3-}. The high pH in the cathode compartment causes immediate precipitation of the phosphate in the liquid and consequently it is hypothesized that precipitation at the electrode surface hardly takes place. After crystallization, a final separation by centrifugation, settling or filtration enhanced by seed crystals or sand allows the final recovery of phosphate compounds [21].

5.3. Material and methods

5.3.1 Material and experimental setup

Nanofiltration concentrate was produced by filtration of permeate from an aerobic pilot-scale MBR that was fed with domestic wastewater withdrawn from the local sewer system. The MBR employed flat sheet Kubota membranes (nominal pore size: 400 nm) running at a flux of 15 L m^{-2} hr^{-1}. The MBR permeate was filtered by cylindrical 400 mL Amicon type dead-end filtration cells containing flat sheet nanofiltration membranes (NF 245 Dow™ Filmtec™) with a total membrane area of 0.0044 m^2 (operating pressure: 5 bar). The remaining concentrate in the cell was used for the experiments. In this manner the MBR effluent was filtered up to a concentration factor of 3-4, a practical limit in the stirred Amicon cells related to fouling of the NF membrane by the MBR permeate. The NF concentrate had a pH of 7.8, no precipitation was observed.

5.3.2 Electrochemical precipitation

The EPR cell consisted of two acrylic glass chambers, a platinum anode in one chamber, a steel cathode plate in the other chamber (electrode area: 0.0022 m^2 each) and a total liquid volume in the cell plus the buffer tanks of 400 mL. 200 mL nanofiltration concentrate was filled in each chamber (incl. compartment and subsequent buffer tank) and circulated through the anode and cathode compartment respectively (Fig. 5.1). Electrical current was applied by a power supply (ES 015-10, DELTA ELECTRONIKA, The Netherlands). 10 and 50 mA were chosen for the experiments with an applied voltage of 3 V. Mainly the duration of the applied current determined the pH.

Both electrodes in the electrochemical cell were separated by the use of a 0.0022 m^2 Fumasep® FKS cation exchange membrane (CEM) (FuMA-Tech GmbH, St. Ingbert, Germany) to prevent the migration of anions (e.g. PO_4^{3-}) from anode to cathode. More importantly, due to the CEM the OH^- produced at the cathode does not migrate to the anode. Although the protons produced at the anode can freely migrate from the anode to the cathode compartment, neutralization of the pH was not expected because even at pH = 8 (the lowest pH used in these measurements) the proton concentration (10^{-8} M) (Table 5.2) was very low compared to the concentration of other cations, like Ca^{2+}, Na^+, K^+, and Mg^{2+} (10^{-3}-10^{-4} M) (Table 5.2).

Both buffer tanks were open to the atmosphere for gas release, for pH measurements (SenTix 41, WTW, Germany) and for sampling. The cathode buffer tank was used as a settling tank for calcium phosphate precipitates. As these experiments were non-continuous batch tests to evaluate the potential of the concept for phosphate recovery, only the NF concentrate in the cathode chamber was addressed. Nevertheless, in a continuous process the full stream could be treated, as in that case, it would first pass the anode followed by the cathode.

In the batch system the NF concentrate was introduced not only into the cathode but also the anode compartment. This was done to balance the ion concentrations and the conductivity in both electrode compartments to avoid diffusional transport due to large differences in ion concentrations. The NF concentrate in the two separated electrochemical cell chambers was circulated by a peristaltic pump (Masterflex®) at a recirculation rate of 5 mL min^{-1}, until the target pH was measurable in the cathode buffer tank and precipitation was induced. The batch time for the total volume of 200 mL (volume per tank divided by the recirculation rate) was 40 minutes. As approximately 50 mL were in the circulation loop (tubes + electrochemical cell), a pH increase and therefore very high removal rates were already detectable in the buffer tank after 15 minutes. Experiments with a target pH of 8.25, 8.5 and 9 were carried out at a current of 10 mA (3V) (current density of 4.6 A m^{-2} or $3.03 \cdot 10^{-4}$ A cm^{-3} per electrode compartment). The test at pH 9 (10 mA) was repeated as triplicate. A higher current of 50 mA (3V) (current density of 22.7 A m^{-2} or $1.5 \cdot 10^{-3}$ A cm^{-3} per electrode compartment) was needed to achieve pH 10 or 11. All experiments were run for a minimum of 2 hours at each target pH level, which was reached after 15-30 minutes depending on the current applied. The current was kept constant until the desired pH was reached. Phosphate recovery efficiency was derived from the observed phosphate depletion in the cathode liquid.

5.3.3 Ion and TIC analysis

For analysis, the NF concentrate from the cathode compartment before and after the EPR experiment was filtered with a 0.45 µm membrane filter to separate the solids from the solution. Concentrations of anions and cations in the remaining liquid were measured. Anions were measured with ion chromatography (Compact IC 761, Metrohm). Cations were analyzed with inductively coupled plasma (Optima 5300 DV, Perkin Elmer). Total inorganic carbon (TIC) content of the NF concentrate before and after the experiments was determined by TOC-VCSH (Shimadzu). For this all inorganic carbon species were transferred to CO_2 and analyzed. Analytical software (Visual MINTEQ 3.0) was used to indicate potential saturation and ion activities in the NF concentrate at different pH. This calculation includes inorganics but does not account for organics as for instance humic acids. Recovery of phosphate and removal of all other compounds describes the depletion from the feed solution (Inflow – remaining solution after treatment).

5.3.4 ATR-FTIR and XRD

After each experiment ATR-FTIR was performed to analyze the functional groups on the surface of the precipitate with a Shimadzu 4800-s ATR-FTIR spectrometer. Precipitates were obtained by filtration through a 200 nm filter (Isopore^{TM}, Merck Millipore). The ATR-FTIR spectra were determined at a spectrum resolution of 2.0 cm^{-1} and 100 scans. Precipitate samples were analyzed with X-ray powder diffraction (XRPD) to clarify the crystal structure. Samples were collected at four different pH levels (pH 8.25, 8.5, 9 and 10). The X-Ray powder diffraction spectra show the 2θ of the crystalline phases. The patterns were recorded in a Bragg-Brentano geometry by a Bruker D8 advanced diffractometer equipped with a Vantec position sensitive detector. The data collection was carried out at room temperature using monochromatic Co Kα radiation (λ = 0.179026 nm) in the 2θ region between 20° and 120°. The step time was 1 second. The sample was placed on a Si {510} times new substrate and rotated during measurement. Data evaluation was performed using the Bruker program EVA.

5.3.5 SEM analysis

SEM-EDX analysis and pictures of the precipitates was made using a Scanning Electron Microscope JEOL-6480LV (JEOL Ltd., Tokyo, Japan) to analyze size and shape of the precipitation. All samples were coated with a thin (10 nm) gold layer (JEOL JFC-1200 fine coater) before observation under high vacuum at 10 kV.

5.4. Results and discussion

5.4.1 Nanofiltration concentrates

Average concentrations of relevant dissolved constituents in the produced nanofiltration concentrates are shown in Table 5.2. With about 5 mg L^{-1} of PO_4^{3-}-P in the feed for the NF (i.e. MBR permeate), the phosphate content in the NF concentrate (to be fed to the EPR) was as expected around 23 mg L^{-1}. These NF concentrate solutions were used as feed for the EPR. The average molar ratio of Ca/P of 2.6 shows a desired excess calcium concentration available for precipitation, compared to the needed Ca/P ratios in common precipitates (Table 5.1). An exception was the experiment at pH 10, where the Ca/P ratio was 1.8. Nevertheless, this is still sufficiently high to obtain all of the mentioned phosphorous precipitates (Table 5.1). These variations in concentration of the NF concentrate occurred because the concentrates were individually prepared in batch tests (in Amicon filtration cells) from real domestic wastewater.

Table 5.2 *Average constituent concentrations in the NF concentrates used in the EPR process and average NF rejections (%) of each of the compounds during NF concentrate production.*

Component	Average concentration in NF concentrate	Average Rejection by NF (%)	Unit
pH	7.8 ± 0.1	-	-
[Na^+]	130 ± 46	25	mg L^{-1}
[K^+]	22 ± 14	7	mg L^{-1}
[Inorg. carbon]	58 ± 8	83	mg L^{-1}
[Mg^{2+}]	22 ± 4	34	mg L^{-1}
[Ca^{2+}]	83 ± 10	29	mg L^{-1}
[PO_4^{3-}-P]	23 ± 10	85	mg L^{-1}

5.4.2 Phosphate recovery from NF concentrate

Fig. 5.2 shows the phosphate recovery at pH 8.25, 8.5, 9.0, 10.0 and 11.0. The operation with a cathode pH of 8.25 yielded approximately 70% phosphate recovery, pH 8.5 yielded 74% recovery, pH 9.0 about 90% and pH 10.0 and 11.0 both gave recoveries of 96%. This increase in recovery efficiency with pH is caused by increasing supersaturation for phosphate precipitates at higher pH [22]. Fig. 5.2 shows that operation at low current (10 mA) was already sufficient to recover considerable amounts of phosphate at a pH of 9 or higher.

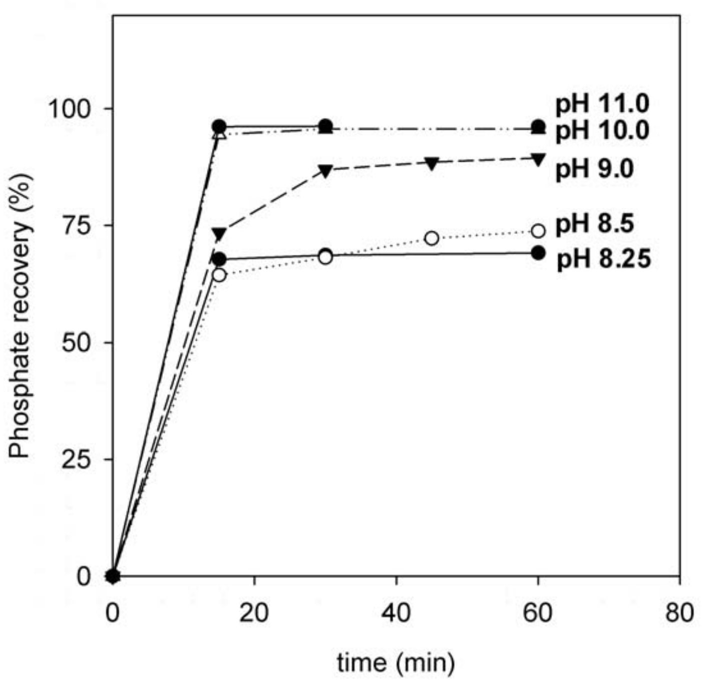

Fig. 5.2. *Phosphate recoveries from the NF concentrate measured over time at different target pH values. Standard deviation for experiments performed at pH 9 was 1.6%, which is considered to be a representative value for all experiments.*

On average, 0.4 - 0.6 mmol L^{-1} (38 - 57 mg L^{-1}) of phosphate was recovered from the solution, except at pH 10 where 1.23 mmol L^{-1} (117 mg L^{-1}) was recovered due to the mentioned higher initial phosphate concentration. Overall, the current efficiency for the recovery of phosphate decreased with increasing pH (pH 9, 10 mA: 53%; pH 11, 50 mA: 19%). Neutralization of the electrolytes due to H^+ migration was not found.

5.4.3 Precipitate composition

Fig. 5.3 shows the molar Ca/P ratio of the precipitate that was recovered from the cathode compartment. This ratio increased with increasing pH from 0.95 at pH 8.25 up to 2.63 at a pH of 11. This increase with pH can be explained by an increasing (as calcium) carbonate ion removal (0, 1.5, 2.2, 17.9 and 25 mg L^{-1}, respectively) from the solution at increased pH values (Fig. 5.4).

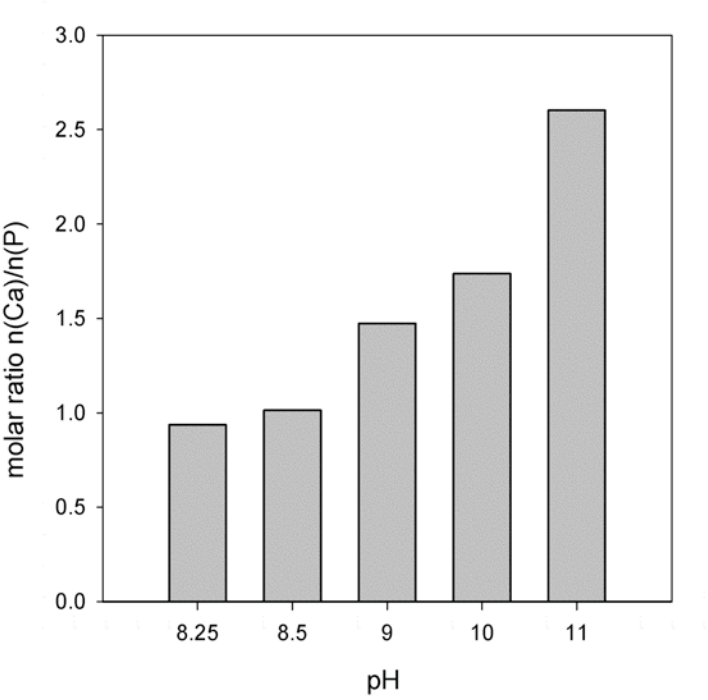

Fig. 5.3. *Molar ratios of calcium to phosphate of the precipitate recovered from the EPR and calculated from concentration changes in the cathode liquid after experiments with different pH. Standard deviation of the experiments performed at pH 9 was 0.5, and this value is considered to be representative for the other experiments as well.*

Fig. 5.4 shows that carbonate removal indeed increased with pH from zero at pH 8.25 up to a maximum carbonate removal of 44.6% observed at pH 11 (Fig. 5.4). This also shows that the calcium removal from the solution does not exceed 30% up to pH 9, which is desired to be able to still improve the bioflocculation by the recirculation of this NF concentrate to the MBR. The formation of calcium carbonate is supported by the ATR-FTIR results shown in Fig. 5.6.

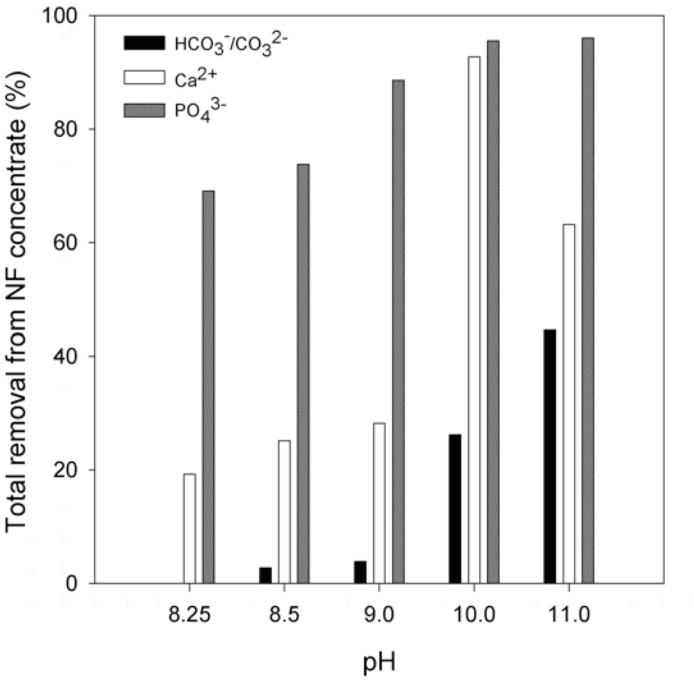

Fig. 5.4. *Phosphate, (bi-)/carbonate and calcium removed (%) from NF concentrate at different pH. Standard deviations for removal experiments at pH 9 were 19% removal for calcium, 28% recovery for phosphate and 5.9% removal for carbonates. These values are considered to be representative for all experiments.*

An additional experiment at pH 9 demonstrated that an increase in current to a value of 50 mA (current density 22.7 A m^{-2} or $1.5*10^{-3}$ A cm^{-3} per electrode compartment) instead of 10 mA (current density of 4.6 A m^{-2} or $3.03*10^{-4}$ A cm^{-3} per electrode compartment) induced a 3.4 times higher carbonate removal but did not impact phosphate recovery. This remained equally high at a value of 91% at pH 9 for both currents. Conclusively, the operation at a higher current does not enhance the phosphate recovery. Besides that, operation at higher currents the pH control was more difficult to control as the pH tended to overshoot the target pH, leading to higher amounts of undesired calcium carbonate incorporation in the product.

Another risk of the higher current (50 mA) is the possible formation of undesired amounts of chlorine gas at the anode due to the oxidation of HCl. The average chloride content in the NF concentrate in both compartments was 135 ± 28 mg L^{-1}. However, it was found that the chloride ion concentrations in the cathode solution did not change significantly over the entire pH range, while the chloride concentration in the anode solution only started to decrease at pH 10 (3% decrease) and 11 (7% decrease) (both at 50 mA). Conclusively, chlorine gas formation was not significant at pH values up to 9 and at the lower currents. At the same time, phosphate recovery under these conditions was high.

The phosphate concentrations in the anode compartment stayed constant, whereas calcium concentrations in the anode decreased significantly. This shows that the presence of the cation exchange membrane prevents the migration of phosphate ions from cathode to anode, while calcium was able to migrate through the CEM. This proof of principle therefore demonstrates that the EPR system has a natural balancing effect and can potentially be used in a continuous mode in an integrated MBR NF/EPR system for simultaneous wastewater treatment and phosphate recovery.

5.4.4 XRD and ATR-FTIR analysis of precipitate

XRD (Fig. 5.5) and ATR-FTIR (Fig. 5.6) spectra were analyzed to obtain more details about the formed precipitates from the EPR and available for phosphate recovery. Since a molar Ca/P ratio in the precipitate of approximately 1 was reached at lower pH (8.25 and 8.5), especially at these pH values crystalline phosphate-containing minerals with a similar ratio like brushite or monetite were expected to form (Table 5.1, Fig. 5.3).

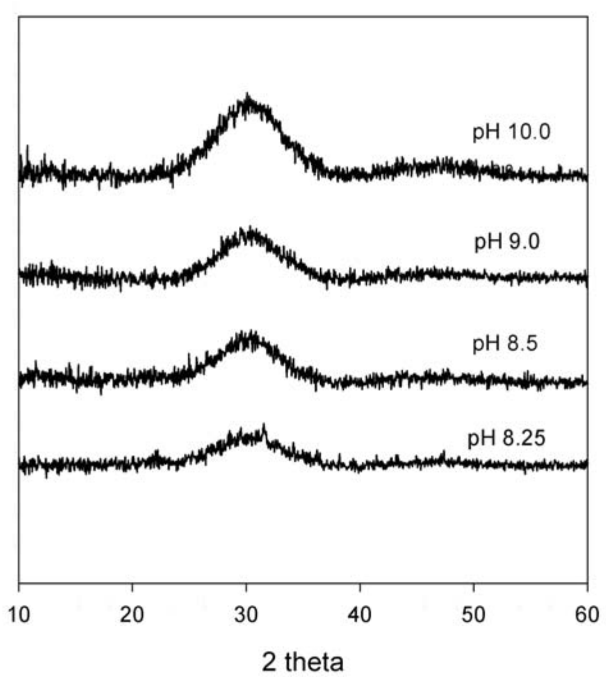

Fig. 5.5. XRD patterns of the phosphate precipitates obtained from the EPR with real NF concentrate at different pH.

In the XRD spectra, crystalline phases would show a distinct, sharp peak. In this case such peaks were not observed, suggesting the absence of crystalline calcium phosphate phases like monetite, OH^- apatite or brushite [23, 24]. Instead, a single broad peak with a maximum at a

2θ angle of 30° was found at all pH levels. A similar XRD peak was found before when using chemical precipitation resulting in ACP formation, occurring at a higher pH of 10.5 [25]. This indicated that the precipitates consisted of an amorphous phase. Regarding the composition (Fig. 5.4), the precipitates contain mainly calcium, phosphates and carbonates, therefore ACP ($Ca_3(PO_4)_2{\cdot}3H_2O$) or amorphous calcium carbonate (ACC) formation is most likely. The calculated saturation indices at pH 8, 9 and 10 (HAP: 13.8, 17.2, 19.2; ACP: 3.2, 4.8, 5.5) show that HAP was much more likely to form solids material than ACP. However, formation of ACP is kinetically faster than that of the strongly bound crystalline HAP. These findings were confirmed by ATR-FTIR. Also here no distinct peaks for crystalline phases like brushite were found (Fig. 5.6).

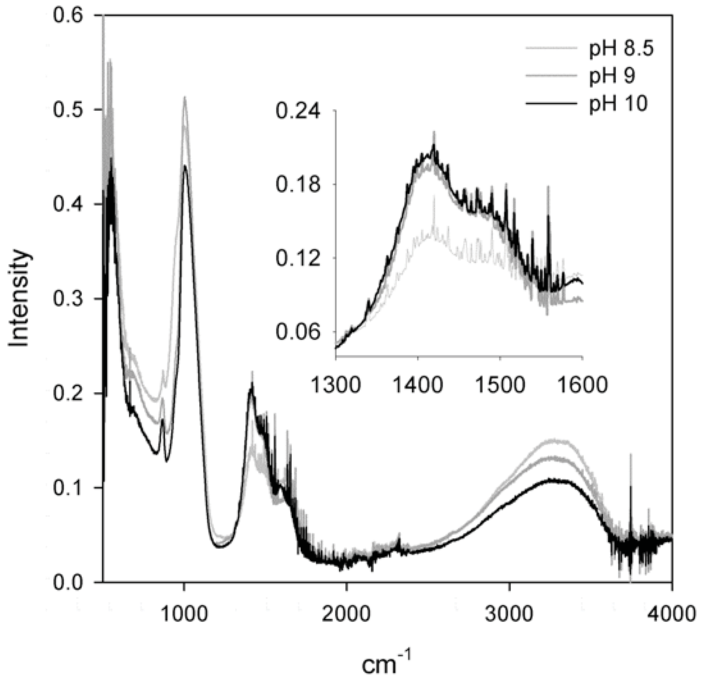

Fig. 5.6. ATR-FTIR spectra of the precipitates from the EPR formed at pH 8.5, 9 and 10, obtained from real NF concentrate.

The spectra presented for pH 8.5, 9 and 10 (Fig. 5.6) contained vibration modes of P-O-H groups of the octahedral PO_4^{3-} and Ca-O units at 1,020 and 555 cm^{-1}, respectively. The peaks in the regions between 3,000-4,000 cm^{-1} and 500-600 cm^{-1} represent the H_2O/OH and Ca-O vibrations, respectively. In accordance with the XRD results, ACP shows a typical asymmetric vibration mode of P-O at 950 cm^{-1} in the ATR-FTIR spectra, which is partly overlapped by the peak at 1,020 cm^{-1} belonging to the stretching vibrations. The vibration bands of water at 1,650 cm^{-1} show the inter-structural water phases in ACP, i.e. as in $Ca_3(PO_4)_2{\cdot}2H_2O$. Both, FTIR and XRD confirm the formation of the commonly metastable phase ACP. ACP usually transforms over time to crystalline minerals like apatite or brushite, depending on the applied pH and concentrations. However, as mentioned, the typical band in the ATR-FTIR for brushite at 959 cm^{-1} was not detected [26].

Regarding carbonates, vibration bands of 1,420 and 1,467 cm^{-1} in the ATR-FTIR spectra can be attributed to vibration modes of carbonate ions and also the small peak at 874 cm^{-1} represents Ca-OH vibration, which is typical for ACC. Nevertheless, the XRD spectra showed no evidence of amorphous calcium carbonate [27], where a small peak residing at 45° 2θ angle would have been expected (Fig. 5.5). The carbonate ions were therefore either incorporated into the ACP or precipitated as a separate amorphous calcium carbonate phase [28].

The different intensities in the ATR-FTIR spectra of the carbonate peaks at 1,420 and 1,467 cm^{-1} indicate qualitative differences, which could be related to the obtained varying carbonate to phosphate ratios (Fig. 5.4). Since ATR-FTIR methods measure rather at the surface of the precipitates, it might be possible that vibration bands of CO_3^{2-}-ions represent surface precipitated calcium carbonate or CO_3^{2-}-ions adsorbed to the ACP, which also may have additionally occurred during the drying period of the filtered samples. Sharp peaks of the more crystalline carbonate phases like calcite and aragonite in the ATR-FTIR at 714 cm^{-1} and 750 cm^{-1} were not observed. The absence of these peaks further confirms that the dominant carbonate precipitate was ACC. The calculated supersaturations for pH 8-11 showed also for carbonates that the amorphous phase was slightly less saturated than the crystalline phases. Considerable amounts of CO_3^{2-} and Ca^{2+} were available in the solution to form ACC but the content in the precipitate remained relatively low. Fig. 5.4 shows that the ACC content in the precipitate was always lower than the ACP content. Even at high pH (11) ACC was 2 times lower and at low pH (8.25) it was even 20 times lower. Conclusively, up to pH 9 the precipitate consisted almost exclusively of ACP. Another explanation for the low ACC content is that phosphate may have acted as an anti-scalant for calcium carbonate. PO_4^{3-} is known to prevent calcium carbonate scaling on numerous surfaces e.g. on pipes in sewage systems by replacing the carbonate ions in the precipitate [29], which can be explained by a competition between phosphate and carbonate ions for calcium. However, the activities of the dominant carbonate species at pH 8-10 are still estimated to be at least 2 times higher than those of the HPO_4^{2-} ions. Moreover, the kinetic preference of ACP in this research consumes large part of the Ca^{2+}-ions and in this way lowers the supersaturation for ACC precipitation.

Reason for the hindered crystallization of the amorphous phase into the crystalline phase is the presence of species such as magnesium, carbonates and humic acids in the NF concentrate. Those could have promoted the stabilization of ACP [20, 30-32]. Chemical analysis confirmed the presence and removal of total organic carbon, CO_3^{2-} and Mg^{2+}-ions from the solution. Molar ratios of magnesium to calcium between 0.37 and 0.76 were found in the NF concentrate. This ratio is sufficient to cause this inhibition and could explain the stabilization of the amorphous phase [33]. Although only limited information on the inhibition mechanism itself is available, the mentioned compounds might have reduced the rate of dissolution and transformation into more crystalline phases. This shows that NF concentrates from a domestic MBR NF process could be a good basis for phosphate recovery in the amorphous phase instead of a crystalline phase, which may have advantages that will be discussed later on.

5.4.5 SEM analysis

SEM-EDX analysis showed that the main elements found in the precipitate were calcium, phosphorous but also magnesium, oxygen and silica. Also carbon, sodium, chloride and potassium were detected. Heavy metals were neither detected in this particular concentrate (by ICP) nor in the precipitates by SEM-EDX analysis. Particles smaller than 1 micrometer were found (Fig. 5.7).

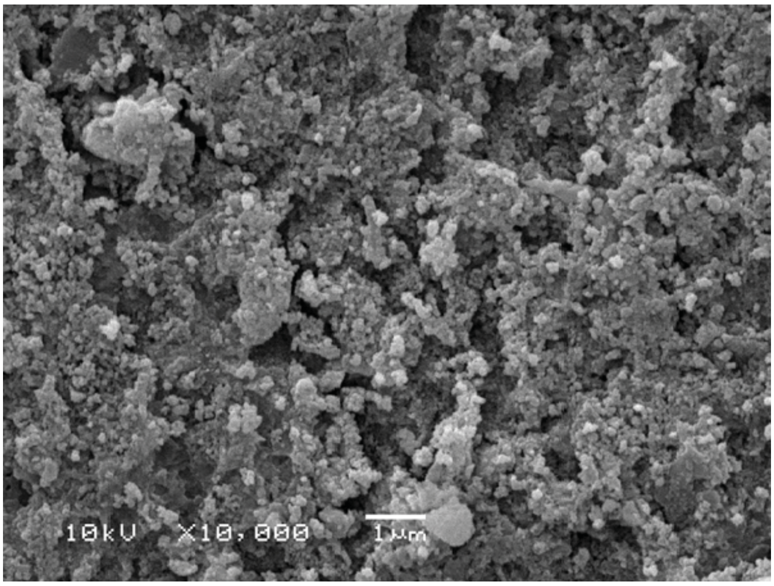

Fig. 5.7. *SEM image of the dried precipitate gained at pH 10 (50 mA) at 10 kV; magnification: 10,000x.*

The small size of the particles could indicate poor settling and consequently poorer separation of the solids from the solution, however settling behavior still needs to be evaluated.

5.4.6 Future application and economical evaluation

The experiments presented in this research have been performed in a batch mode. Results show the potential of applying EPR in a continuous mode in an integrated MBR NF/EPR system as presented in Fig. 5.8. The nanofiltration concentrate would first pass the anode chamber to strip CO_2 at acidic pH, followed by an alkaline pH cathode chamber where precipitation is induced.

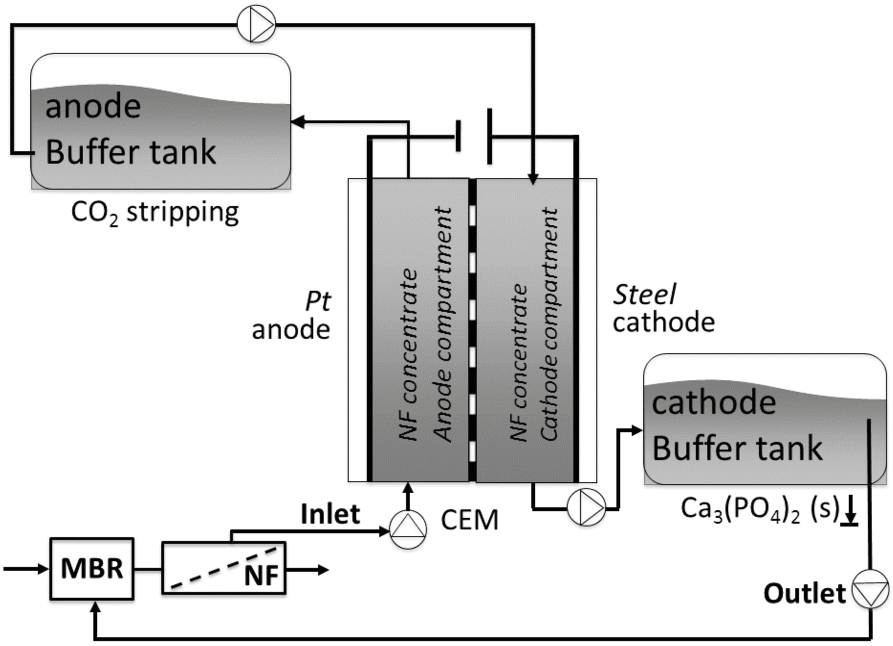

Fig. 5.8. Schematic overview of a continuous electrochemical phosphate recovery (EPR) process.

A great advantage of the approach proposed here is the continuous formation of hydrogen gas bubbles along the cathode surface due to the electrolysis reaction. In the past, similar devices built for water softening [15, 18] had the major concern of formation of calcium phosphate, carbonate or hydroxide precipitation at the cathode surface. Also in our case the high concentrations of carbonates especially at higher pH could theoretically cause scaling. Nevertheless, no deposition on the electrode surface was visually observed. H_2 formation was visually observed during the experiments and suggested to prevent scaling at the cathode surface. Consequently, this will not decrease the membrane or electrode performance. The calculated H_2-gas production [34] assuming a maximum coulombic efficiency of 100% was only 4.2 mL per hour during the experiments, which is relatively low compared to e.g. 80 mL per hour in microbial electrolysis cells for hydrogen gas production [35] and safety issues are not expected. At a larger scale, the use of H_2 for energy applications could be considered.

Regarding the settleability of the precipitates, the use of for instance HAP seed crystals may significantly enhance the particle size and therefore the settleability [36]. The recovered amorphous ACP could be used as a fast dissolving fertilizer [37]. Phosphate minerals can be found in fast dissolving forms but also in slower dissolving forms (e.g. struvite) [38]. The more crystalline the calcium phosphate phase, the slower the dissolution rate and the slower the release of PO_4^{3-}-ions to the soil, with hydroxyapatite being the most stable and slowest dissolving phase. Solubilities have not been determined in this research but it may be interesting to allocate the dissolution rates of the precipitates in neutral media.

A decrease in carbonate precipitation is expected when this system is operated in a continuous mode with simultaneous CO_2 stripping in the anode compartment. The lower pH of the anode can be used to shift the carbonate speciation towards H_2CO_3 (carbonate precipitation) that can be removed from the water. This avoids contamination of the end product with (co-precipitated) carbonates.

Finally, depending on the wastewater composition, also heavy metals (e.g. transition metals), magnesium, potassium or humic substances can be present in the nanofiltration concentrate and might also be present in the precipitate to a certain extent. Statements from the Crystallactor® technology that only very low amounts of heavy metals were found still have to be carefully evaluated for this process. Depending on the needed purity of the precipitate, other treatment steps, like adsorption, ion exchange, electrolysis or coagulation and flocculation [39] might be needed before reuse. Further research in this regard is required. As carbonates are likely to co-precipitate at high currents and pH values, it depends on the application whether carbonates in the precipitates are acceptable or not and to which extent.

In general, phosphate recovery in the form of ACP from produced NF concentrates (Table 5.2) by using water electrolysis (EPR) is possible, and can be introduced in a continuous MBR NF process, instead of removing phosphates via the waste sludge [9]. Compared to a recovery of 65-70% reached by the Crystallactor® technology [19] this process seems to be more efficient and a high recovery is promoted by the presence of the membrane. Also no transportation, storage and use of chemicals are needed but a fair comparison of a continuously operating system with e.g. the commercially available Crystallactor® technology still has to be done.

An energy-cost estimation (Appendix A) for electrolysis was performed assuming the following operational settings for recovery of one ton of phosphorous: a target pH of 8.5, an applied voltage of 3 V and a current of 0.01 A. The applied voltage of 3 V was needed to run the electrolysis and was higher than the theoretical value of 1.23 V and also higher than the

practical minimum of 1.48 V necessary to overcome the activation energy for water electrolysis. Reason for this high applied voltage was the lower conductivity of the NF concentrate compared to e.g. reverse osmosis concentrates. This also implies that with 3 V applied voltage, parts of the energy were lost as heat. An estimation of this heat loss by 1.52 V showed a negligible temperature increase of 0.07 K per m^3 during the electrolysis.
With an industrial energy price of 0.10 € kWh, the costs related to electrolysis would be 303 € per ton of recovered P (assuming 100% galvanic efficiency). This is well below the costs for phosphorous of 685 € per ton of P (excluding transportation costs) in phosphate rock, assuming a maximum P content of 17.5% in the rock [40, 41], and therefore phosphate recovered by this electrochemical technology may provide an attractive possibility to replace part of the scarce phosphate rock. Also from a wastewater treatment perspective the operational costs related to energy consumption are relatively low, i.e. only 0.004 € per m^3 of treated wastewater, while significant costs can be saved on biological or chemical phosphorus removal.

Table 5.3 shows the energy estimations based on the experimentally gained data for the electrochemical process.

Table 5.3 *Calculated energy (kWh) per kg phosphorous and per cubic meter of concentrate treated based on the experimental P-recoveries at different pH and applied currents.*

pH	8.25	8.5	9	10	11
mA	10	10	10	50	50
kWh kg-P^{-1}	3.0	2.4	2.4	5.0	12.6
kWh m^{-3}	0.054	0.049	0.041	0.195	0.195

These results show that the energy consumption is directly related to the electricity used for the electrolysis. Increased current led to increased energy which also increased the P-recovery. Additionally, at higher currents more energy is needed per kg P as at the same time energy was withdrawn for carbonate co-precipitation.

An additional advantage of this system is that no storage of chemicals is needed. However, the platinum electrode used in this system is expensive, so a cheaper option e.g. nickel electrodes could decrease these costs but will also decrease the robustness and efficiency of the process. In the continuous system also costs for CO_2 stripping and transportation costs of products should be taken into account.

5.5. Conclusions

- Amorphous calcium phosphates can be recovered to a very high degree (up to 90%) from real domestic nanofiltration concentrates with an integrated MBR NF/EPR concept.
- The NF concentrate can be re-introduced into the MBR at much lower phosphate and calcium concentrations, reducing scaling problems in the MBR system. Nevertheless, sufficient calcium should be available to aid the desired bioflocculation in the MBR.
- High phosphate recovery can be obtained at pH = 9, as precipitation of calcium phosphates or carbonates on electrodes or membrane surface is not observed.
- EPR is attractive as no usage, storage and transportation of chemicals is needed.

Acknowledgements

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Appendix A: Energy and cost calculation

The energy calculation in this manuscript is based on the actual moles of P needed for the calcium phosphate formation.

Assuming 1,000,000 g of P: 32 g mol^{-1} gives 31,250 mol P. The phosphate speciation can be assumed according to the following:

The sum (Total PO_4) of the two main present species at pH 7.8 ($H_2PO_4^-$ and HPO_4^{2}) is given as:

Total PO_4 = $TOTPO_4$ = $[H_2PO_4^-] + [HPO_4^{2-}]$

These two species have an equilibrium at a pKa of 7.21, which gives their relationship as:

$[HPO_4^{2-}][H^+] / [H_2PO_4^-] = 10^{-7.21}$

After rearrangement and substitution of the two equations, the moles of

$[H_2PO_4^-]$ and $[HPO_4^{2-}]$ at pH 7.8 can be calculated according to:

$[HPO_4^{2-}] = ([TOTPO_4] * [10^{-7.21}]) / ([10^{-pH}] + [10^{-7.21}])$

$[H_2PO_4^-] = TOTPO_4 – [HPO_4^{2-}]$

$[HPO4^{2-}] = (31{,}250 \text{ mol} * 10^{-7.21}) / (10^{-7.8} + 10^{-7.21}) = 24{,}860 \text{ mol}$

$[H_2PO4^-] = 31{,}250 – 24{,}860 = 6{,}390 \text{ mol}$

Regarding the following reactions that will generate amorphous calcium phosphate,:

$3Ca^{2+} + 2[H_2PO_4^-] + nH_2O \Leftrightarrow Ca_3(PO_4)_2 * nH_2O + 4H^+$

$3Ca^{2+} + 2[HPO_4^{2-}] + nH_2O \Leftrightarrow Ca_3(PO_4)_2 * nH_2O + 2H^+$

From these and the moles of the two species above, the amount of OH^- needed to produce amorphous calcium phosphate precipitation can be calculated:

In total 37,638 M (24,860 M + 2 * 6,390 M) of H^+-ions are released when 1 ton P is precipitated assuming that all P is precipitated. To keep the pH at the cathode equal, a corresponding amount of OH^- is needed to titrate this amount of H^+-ions. One has to produce 37,640 M of OH^-.

Electric charge necessary to produce OH^- needed: 37,640 mol * 96,485 C mol^{-1} = 3.63 x 10^9 C

Energy per ton of P: 3.63 x 10^9 C * 3V (applied voltage) = 1.0895x 10^{10} J ton P^{-1}

Power per ton of P in 15 minutes: 1.0895x 10^{10} J ton P^{-1}: 900s = 1.21 x 10^7 W : 1000 = 12105 kW * 0.25 h = 3026.3 kWh

Costs per ton of P: 3026.3 kWh * 0.10 € kWh^{-1} = **303 € ton P^{-1}**

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6

MBR NF wastewater treatment with NF concentrate recirculation and integrated phosphorus recovery

This chapter will be submitted:

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Abstract

The permeates of membrane bioreactors (MBR) used to treat wastewaters are a solids-free source for phosphorus (P) recovery. Phosphate mining is not a sustainable practice and P is becoming a scarce resource. High P levels in discharged waters must be low to avoid eutrophication. P recovery can be carried out in an integrated MBR NF process with recirculation of the nanofiltration (NF) concentrate. This paper compares the performance of two laboratory-scale MBR NF systems with NF concentrate recirculation, one with and one without P recovery, operated for 200 days. As reference, a “blank” MBR, without a subsequent NF membrane or P recovery step was used. For both systems with NF concentrate recirculation, the resulting NF permeate has a sufficiently low P level that allows discharging it, but also makes its reuse possible, for instance as cooling water in power plants or for irrigation purposes. NF concentrate recirculation causes increased scaling, especially on the NF membrane, but the addition of a P recovery step clearly shows decreased scaling. The P recovery step significantly improved the filterability of the MBR permeate by the NF membrane, which allows sustainable production of reusable water.

6.1 Introduction

The removal of phosphorus (P) from wastewater is essential as the discharge of wastewater containing too much P causes eutrophication. To protect the environment, in sensitive areas which are subject to eutrophication, the EU’s concentration limit for discharge from wastewater treatment plants is 1 to 2 mg P L^{-1} for total phosphorus [1], signifying a P removal of 80% or more. Wastewater can be treated in a membrane bioreactor (MBR) and transformed into reusable water when a tertiary treatment such as nanofiltration (NF) is applied. Nanofiltration produces a concentrated waste stream, but previous research investigated the possibility to recirculate it to the MBR [2, 3].

P, however, is becoming a scarce nutrient [4] and phosphate mining is not very sustainable, making P recovery increasingly important. An advantage of NF concentrate recirculation is that the very high rejection of P by the NF membrane makes it possible to eliminate conventional chemical or biological P removal and introduce a P recovery step instead. Without this P recovery step, NF concentrate recirculation would cause calcium phosphate precipitation [3]. P scaling was also observed by Joss et al., who used a reverse osmosis polishing step after the MBR [5]. A possible drawback of using RO instead of NF is the high salinity of RO concentrate, which may also negatively impact the biological performance of the MBR. NF concentrates have a much lower salinity, and therefore have no or little influence on the biological processes in the MBR [6] in terms of osmotic pressures and deflocculation.

In principle, the most obvious location for P recovery is the NF concentrate stream as that contains the highest P concentration. However, in earlier research [3], we showed that the increased P concentration due to concentrate recirculation impacted especially the NF operation and scaling in the form of calcium phosphate precipitation on the NF membrane occurred. Considering this, recovery of P from the MBR permeate preceding the NF operation is probably more effective in terms of reusable water production.

The research presented in this paper evaluates the performance of three laboratory-scale MBRs over a period of 200 days and investigates the effectiveness of an integrated MBR NF process with concentrate recirculation and P recovery on the quality of the produced water, the possibilities for P recovery and the MBR and NF membrane performance. The first MBR was used as a blank reactor; its permeate was discharged without any subsequent NF filtration or other treatment. The other two systems included an NF step with NF concentrate recirculation. One of these systems also included P recovery from the MBR permeate. We present details on the performance of these three systems, the quality of the NF concentrates and of the MBR and NF permeates. We determined the loss of P as scaling or in the sludge. The impact of the P recovery step on NF performance was investigated in more detail by dead-end filtration tests.

6.2 Experimental approach

6.2.1 MBR setups

Three identical seven-liter MBRs (Fig. 6.1) referred to as R100% (MBR NF with 100% concentrate recirculation), R100%-P (MBR NF with 100% concentrate recirculation and P removal from the MBR permeate) and R0% (MBR, without concentrate recirculation or P removal) were run over a period of 200 days. The municipal wastewater inflow was 36 L day^{-1}, the temperature of the MBRs was stable at 19 ± 1 °C, and the sludge retention time was set to 16 days in each of the three MBRs. Filtration was operated at a continuous regime of eight minutes filtration and two minutes relaxation, leading to a hydraulic retention time of 4.7 hours.

In earlier research [3], increased calcium phosphate precipitation impacted especially the NF operation. To minimize this (and have more P available for recovery), the pH in the MBRs was automatically kept at 7.3 with 1.2 M HCl (VWR BDH Prolabo). In this manner we were able to maintain higher dissolved phosphate concentrations, e.g. 9.8 ± 2.9 mg L^{-1} in the R100% MBR permeate.

Transmembrane pressure was recorded automatically via pressure sensors (Cerabar M, Endress+Hauser). Coarse bubble aeration plates were installed for simultaneous aeration of biology and membranes. The dissolved oxygen concentration was controlled at around 2 mg L^{-1} by simultaneously dosing compressed air and nitrogen gas. As the total gas flow supplied to each of the three reactors was 0.6 m^{3} hr^{-1} m^{-2}, the shear rate in the reactors was also identical. No anoxic or anaerobic stages were applied, i.e. biological P removal and denitrification were not implemented.

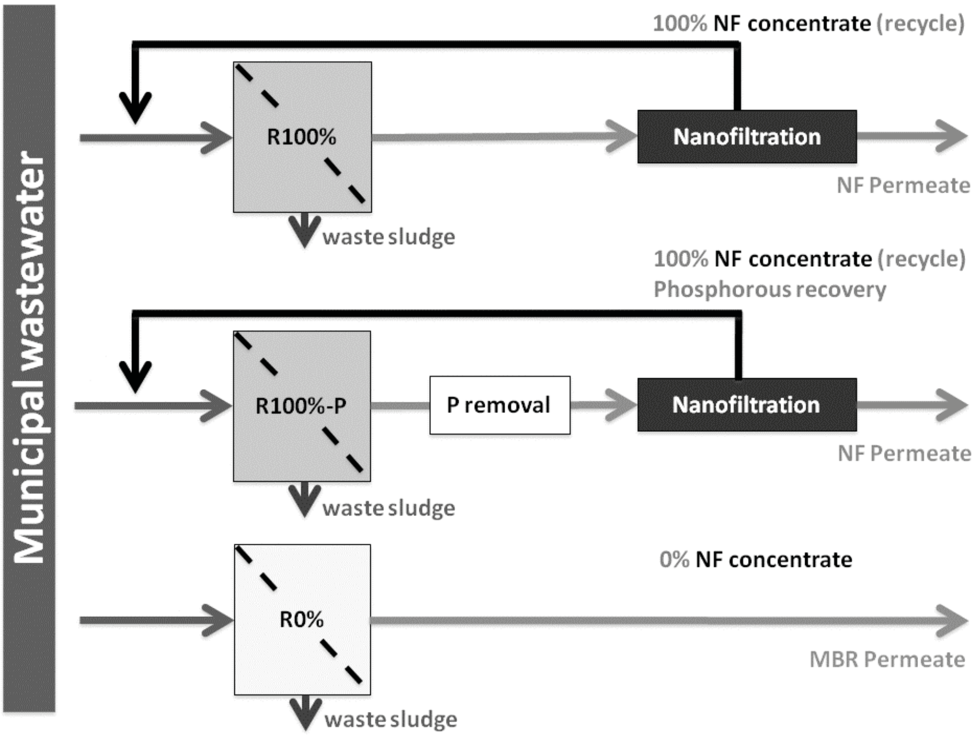

Fig. 6.1. *MBR NF reactor setup: Reactor R100% was operated with full NF concentrate recirculation, reactor R100%-P was operated with full NF concentrate recirculation and included a P-recovery step after the MBR, and reactor R0% was run without any recirculation or P recovery.*

Municipal wastewater was withdrawn from a nearby sewer system, pre-settled and supplied to all three reactors at 36 L day^{-1}. Two flat sheet microfiltration membranes (Kubota, Japan) (0.116 m^2 per plate, 0.4 μm pore size) were used in each MBR to extract permeate at an average operational flux of 6.4 to 7.5 L m^{-2} h^{-1}. The MBR permeates of the two recirculation reactors (R100% and R100%-P) were collected in 600-L storage tanks and each of these permeates was treated by an NF unit. The MBR permeate of the blank run was discharged.

6.2.2 Nanofiltration and P recovery

The R100% MBR permeate was concentrated to 100 L using a nanofiltration setup containing a 2.5″ spiral-wound NF270 module (DOW, membrane area 2.6 m^2), operated at a feed pressure of 11 bar. MBR permeate was collected in the 600-L tank until NF treatment was performed. In total eleven NF treatments were performed on the following seven operational days (during the first 66 days, concentrate was recirculated, but sampling was not performed): 67, (87 – no data available) 108, 128, 144, 157, 179 and 194 (approximately every two to three weeks). The targeted recovery was 85% of the NF permeate.

A similar NF procedure was performed with R100%-P MBR permeate, but before concentration of the MBR permeate in the NF step, the P was allowed to precipitate in the 600-L tank. As the Ca and P concentrations of the incoming wastewater were relatively high and the recirculation of the NF concentrate further increased these concentrations, calcium phosphate scaling predominantly occurs on the NF membrane during the NF concentration step. To overcome this, the P removal step was introduced in the MBR permeate stream and not in the NF concentrate stream. To this end, 1M NaOH (VWR BDH Prolabo) was added under vigorously mixing to the collected MBR permeate until a pH of 9.5 was reached. The precipitate was allowed to settle overnight. After precipitation, the supernatant was transferred into another 600-L tank, and the pH was readjusted to 7.3 with pure 37% HCl (VWR BDH Prolabo). The “P-free” MBR permeate was then further treated by a second NF270 module at a feed pressure of 11 bar (NF stage in the MBR NF process).

The resulting 100-L batches of NF concentrate were fed back continuously to their respective MBRs at a flow rate of 6.5 L day^{-1} (together with 36 L day^{-1} of municipal wastewater) over a period of two to three weeks until the next MBR permeate batches were collected and could be processed by the subsequent NF. The recirculated NF concentrate represented 15 vol.% of the total inflow of the two recirculation reactors. The blank MBR (R0%) was run without a subsequent NF step (wastewater equaled 100% of the inflow). R0% MBR permeate was directly discharged into the sewer.

6.2.3 Cleaning

MBR cleaning was performed whenever one of the MBRs exceeded a transmembrane pressure of 400 mbar. One of the two recirculation reactors always reached this threshold sooner than the blank reactor, and determined the cleaning frequency. In all cases, all membrane plates were cleaned at the same time (approximately biweekly). After stopping MBR operation, physical cleaning was performed by gently wiping the membrane surfaces with a sponge. Subsequently, chemical cleaning was performed by soaking the membranes in 0.2 g L^{-1} NaOCl for 2 hours followed by rinsing with tap water. NaOCl cleaning was followed by 2 hours immersion in 1.25 g L^{-1} citric acid, and a rinse with tap water before reinstallation.
NF membrane cleaning was performed after each concentrate production run at low transmembrane pressure (2 bar). Citric acid (adjusted to a pH of 4) was used to rinse the installation for 10 minutes, followed by a rinse with tap water for 10 minutes. Citric acid is an effective cleaning agent for removing calcium phosphate scaling and restoring the flux in NF units [7].

6.2.4 Analytical methods

Sampling was performed on sixteen operational days (days 59, 66, 79, 87, 93, 100, 107, 114, 121, 128, 135, 142, 156, 163, 177 and 193) for the continuous MBR NF setup and on days 67, 108, 128, 144, 157, 179 and 194 during NF concentrate production. The presented P concentrations in the R100% and R100%-P MBR permeate (Fig. 6.2) and the NF concentrates (Fig. 6.3) result from sampling during NF treatment. The P concentration presented for R0% MBR permeate and the wastewater are grab samples, representing the actual concentration on that specific day of the measurement. Element concentrations were measured in 0.45 µm prefiltered wastewater, as well as MBR tank and permeate and NF permeate and concentrate, using inductively coupled plasma with optical emission spectroscopy (ICP-OES, Optima 5300 DV, Perkin Elmer).

Once a week, total suspended solids (TSS) and volatile suspended solids (VSS) concentrations were measured according to standard procedures [8]. In addition, 50 mL sludge samples were taken on days 38, 106, 120, 134, 156 and 178 and then centrifuged for one minute at 3500 rpm. 0.5 g of the resulting pellets was digested with 10 mL of nitric acid (65 wt%, VWR BDH Prolabo) for 45 minutes at 180 °C in a microwave digestion oven (Ethos One, Milestone). Element concentrations were subsequently determined with ICP-OES (Optima 5300 DV, Perkin Elmer). The TSS of the 0.5 g of sludge was determined as well to be able to present the data per g TSS. The average values presented (mg $gTSS^{-1}$) are averaged over all these single measurements.

The chemical oxygen demand (COD) and ammonium content and the corresponding removal percentages (difference between inflow and permeate) were determined as well. All concentrations were automatically analyzed using Hach Lange test kits (Hach Lange GmbH), using a DR 3900 VIS spectral photometer (340 - 900 nm). Total COD in the wastewater and MBR permeate was measured without additional filtration. For ammonium measurements, the wastewater and MBR permeate samples were first filtered with a 0.45 µm membrane syringe filter (PTFE, Cronus) to avoid photometrical interferences. Decrease of COD and removal of ammonium were calculated from the concentrations in wastewater and MBR permeate. Due to variations in the municipal wastewater composition in time, the experimental standard deviations were relatively large but reasonable.

To analyze the elemental composition of the precipitate from the P recovery step, a sample was taken after 179 days of operation from the bottom of the MBR tank and centrifuged for 2 minutes at 1,000 rpm. The remaining solids were then dried and analyzed using the energy-dispersive X-ray spectroscopy (EDX) option of a JEOL-6480LV (JEOL, Japan) scanning electron microscope (SEM). All samples were coated with a thin (10 nm) gold layer (JEOL JFC-1200 fine coater) under vacuum and examined at an accelerating voltage of 6 kV or 10 kV. Membranes were imaged as well, following the same procedure.

6.2.5 Filtration of MBR permeates

NF filterability of the MBR permeates was tested in stirred dead-end filtration cells using new flat sheet NF270 membrane samples. MBR permeates were taken straight from the MBRs and received no further treatment; the similar pH of all three permeates was the result of the pH adjustment during the continuous operation. After determination of the clean water fluxes, 400 mL of the three MBR permeates were filtered at 5 bar. Tests were carried out with MBR permeates sampled on day 164 and day 180 to check reproducibility, but only results for day 164 are shown in this paper. The two tests produced similar results in terms of NF resistance; the exact values differed slightly because of the changing composition of the municipal wastewater. The mass of each of the collected permeates was recorded by an automated weighing system. Resistances were calculated from the flux, the applied pressure and the viscosity. Viscosity of the MBR permeate was assumed to be equal to that of water and was corrected to a standard temperature of 20 °C. Elements in feed and permeate were determined by ICP-OES.

6.2.6 Filtration of MBR permeates after P recovery at different pH values

In a second test, 1,200 mL of the R100% MBR permeate was collected directly from the reactor and separated into three fractions of 400 mL each. The pH in these three samples was adjusted to 8, 9 and 10 by addition of 1 M NaOH to induce calcium phosphate precipitation. Subsequently, the samples were centrifuged at 3,000 rpm for three minutes and the pH in the remaining liquids of all three samples (now containing different amounts of P in solution) was readjusted to pH 7 with 1M HCl to assure equal pH conditions during filtration. Filtration was performed in stirred dead-end filtration cells at 5 bar over fresh NF270 membranes, after determination of the clean water flux. Flux and permeate composition were determined as described in Section 6.2.5.

6.3 Results and discussion

6.3.1 MBR reactor performance

In the MBRs the calculated COD decrease (the difference between wastewater and MBR permeate levels) was 86 ± 6%, 88 ± 5% and 90 ± 5% with COD concentrations in the MBR permeate of 60 ± 18, 52 ± 13 mg L^{-1} and 37 ± 11 mg L^{-1} for R100%, R100%-P and R0%, respectively. This fits with the results of earlier work, in which recirculation was found to worsen NF performance and especially MBR membrane performance [3]. This was confirmed by the transmembrane pressure, which was higher in the systems with recirculation MBRs than in the blank MBR, indicating more fouling in the MBRs with NF concentrate recirculation. However, there was no significant difference between the transmembrane pressures in the R100% and R100%-P MBR.

The MLSS levels were 4.2 ± 1.5 and 4.4 ± 1.2 g L^{-1} for R100% and R100%-P, respectively, whereas a higher value of 5.1 ± 1.2 g L^{-1} was obtained for R0%. The nitrification efficiency in all three reactors always exceeded 95%. This indicates that concentrate recirculation did not have a toxic effect on the biological processes in the MBR. Similar results were found in previous research, which focused on the effect of NF concentrate recirculation on biological performance [6].

6.3.2 Chemical P recovery

6.3.2.1 P removal effectiveness

In the R100%-P system, P was recovered from the MBR permeate, after which this permeate was used as the feed for the NF step. Fig. 6.2 shows dissolved P concentrations in the MBR permeates of the R0%, R100% and R100%-P (after P removal) reactors over time; the dissolved P concentration in the wastewater inflow is also shown.

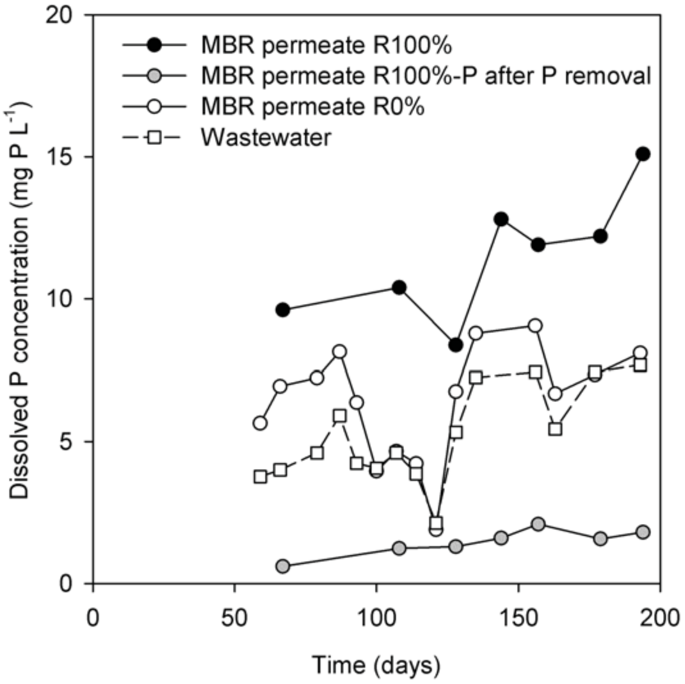

Fig. 6.2. *Dissolved P concentration (mg P L^{-1}) in R100% and R100%-P MBR permeate (after P removal). R100% and R100%-P MBR permeates were sampled during NF treatment and are therefore averages of the MBR permeate collected between two NF concentration tests. For comparison, the dissolved P concentration in the R0% MBR permeate and wastewater inflow are also shown. As no MBR permeate was collected for R0%, the presented values for R0% MBR permeate and wastewater are grab samples, representing the actual concentration at that specific day of the measurement.*

Fig. 6.2 shows that the P removal step lowered the P concentration in the MBR permeate down to 0.6 to 2.1 mg P L^{-1}. Before the P removal step, the P values in the MBR permeate of R100%-P ranged from 4.5 to 6.2 mg P L^{-1}. The values after P removal are close to the EU discharge limit of 1 to 2 mg P L^{-1} (depending on the size of the treatment plant) [1]. By comparison, R100% MBR permeate showed P concentrations of 8.4 – 15.1 mg P L^{-1}, as P was not removed but concentrated in the system. The R0% MBR permeate had P concentrations of 1.9 to 9.1 mg P L^{-1}, which was close to the dissolved concentration in the wastewater (2.1 to 7.7 mg P L^{-1}), as expected. This indicates differences in P uptake by the sludge and therefore differences in the loss of P via the waste (discussed in Section 6.3.2.3).

Fig. 6.3 shows the average P concentrations in the batch-wise produced NF concentrates of R100% and R100%-P that were recirculated to the respective MBR.

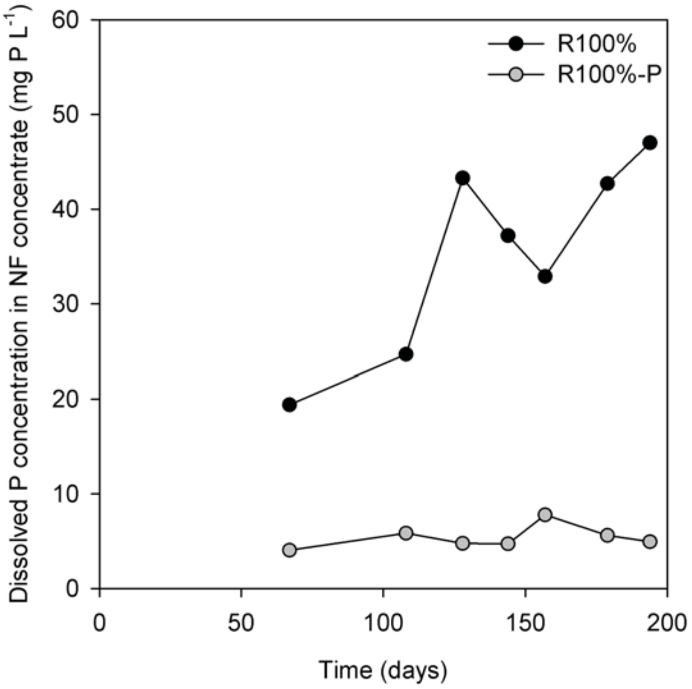

Fig. 6.3. *Dissolved P concentration in NF concentrates (mg P L^{-1}) of R100% and R100%-P. All samples were taken directly after the production of the concentrates by the NF.*

As expected, the P content in the NF concentrate of R100%-P was lower (4.0 to 7.8 mg P L^{-1}) than that of the R100% concentrate (19.4 to 47.0 mg P L^{-1}). The impact on membrane performance will be discussed in the next paragraphs.

6.3.2.2 Effluent quality for water reuse

Conventional P removal processes reduce the P content to approximately 1-2 mg L^{-1} [1]. To assess the effectiveness of the proposed concept and to evaluate the influence of the P recovery step on the NF permeate quality in terms of P, the NF permeate quality of the two recirculation reactors (R100% and R100%-P) and the R0% MBR permeate are determined. Fig. 6.4 summarizes the results.

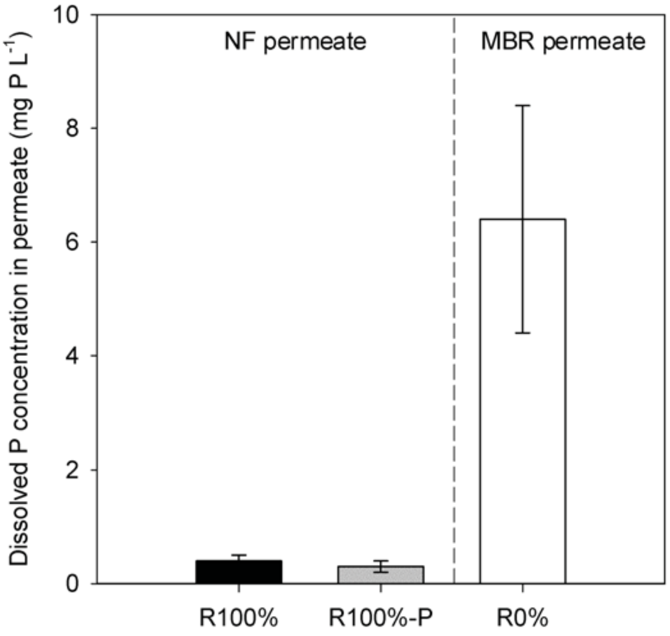

Fig. 6.4. *Average dissolved P concentration (mg P L^{-1}) in the final product of the three MBR systems (NF permeate for R100%-P and R100%, and MBR permeate for R0%). The presented values are the averages of all values gained during NF treatment (R100% and R100%-P) performed during the 200-day operation and averages of grab samples taken on sixteen days for R0% MBR permeate.*

As expected, the MBR permeate of R0% had the highest P content (1.9 – 9.1 mg P L^{-1}) owing to the absence of a P removal step and NF. Even though P was not removed from the R100% MBR permeate, the NF permeates from R100% and R100%-P showed remarkably similar P concentrations of 0.1 to 0.6 mg P L^{-1} and 0.2 to 0.5 mg P L^{-1}. This similarity is due to the high P rejection of the NF270 membrane of 97 ± 2% and 85 ± 12% for R100% and R100%-P permeate, respectively. The lower rejection in the R100%-P NF step may be related to the higher monovalent salt concentration after P recovery; the Na concentration in R100%-P was 193 ± 24 mg L^{-1} due to NaOH addition, but 153 ± 17 mg L^{-1} in R100%. After P recovery, the additional P reduction by the NF filtration step was relatively small. However, NF remains an essential polishing step as it not only removes P, but also divalent ions and organic components, which are essential for water reuse.

The use of NF not only makes it possible to meet the wastewater discharge limit of 1 to 2 mg P L^{1}, but reuse as for example irrigation water or cooling water in power plants becomes possible as well. To reduce the risk of phosphate scaling, the maximum allowed phosphorus value in cooling water is 0.5 mg L^{-1} [9]. The total nitrogen content would have to be below 8 mg L^{-1}, which could be accomplished by a denitrification stage. Nevertheless, for other uses, the level of heavy metals and other micropollutants could be of concern.

Overall, NF delivers a permeate with low ionic and low organic contamination. Applicability needs to be assessed for each specific scenario, for instance the type of plant and the soil in relation to the water quality needs to be considered.

6.3.2.3 Precipitates, P recovery and loss

Average P recovery from the R100%-P MBR permeate upon NaOH addition was on average as high as 71 ± 4%. The precipitated material was collected from the R100%-P MBR permeate tank and, after centrifugation and drying, investigated with SEM EDX (Fig. 6.5).

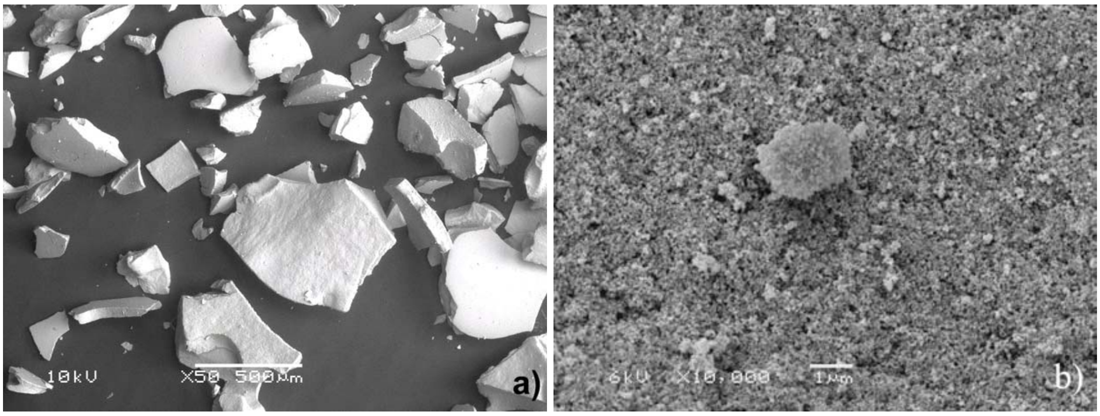

Fig. 6.5. *SEM images of the dried precipitates found in the R100%-P MBR permeate after the addition of NaOH at a magnification of a) 50x and b) 10,000x.*

Fig. 6.5a shows the dried material at a magnification of 50x. At a higher magnification of 10,000x (Fig. 6.5b), the precipitate shows an irregular amorphous structure without larger crystals. This gives the idea that the precipitates contain also organic material which hinders/obstructs the formation of larger crystals. For this reason the elemental composition of the precipitates is further checked with SEM EDX. Table 6.1 summarizes the elemental composition of the material as analyzed by SEM EDX.

Table 6.1 *Composition of the dried precipitates found in the R100%-P MBR permeate after addition of NaOH as determined by SEM EDX.*

Element	**C**	**O**	**Na**	**Mg**	**P**	**S**	**Cl**	**Ca**	**Rest**	**Ca/P**
Atomic %	33.7	51.9	0.3	0.8	4.9	0.1	0.4	7.7	0.2	1.57

The results of the EDX analysis show that Ca and P are the main inorganic species in the precipitate. In addition, a large contribution by either organics or carbonates (containing C or O) was observed. Other elements such as Mg, Na and Cl were also present. Not much can be said about the specific molecular structure of the substances in the precipitate as SEM EDX only provides the elemental composition. Humic acids are likely to adsorb on the precipitate surface or precipitate together with the phosphates (or carbonates) and may explain the percentages of C and O [10, 11]. Heavy metals can contaminate any type of precipitate resulting from wastewater. Although the Cu, Zn and Cr levels are less than 0.03% for each (not shown in Table 1), they might limit the use of these precipitates as fertilizer [12]. Nevertheless, after further processing it may be possible to blend them with other fertilizers [13].

The Ca/P ratio of 1.5 to 1.6, as found after precipitation at pH 9.5, suggests the formation of for instance calcium-deficient hydroxyapatite [14], but no crystalline structures were observed during imaging at higher magnifications. The formation of amorphous calcium phosphates would also fit with the Ca/P ratio of 1.5 ($Ca_3(PO_4)_2H_2O$). The occurrence of amorphous calcium phosphates is related to the presence of humic acids [15] and magnesium [16] in the wastewater as those can hinder crystallization, but incorporation of amorphous calcium carbonates cannot be excluded either.

The occurrence of calcium phosphate scaling on the NF membrane is not only disadvantageous in terms of membrane operation; it also reduces the amount of P that is available for recovery. In R100%, the P lost on the NF membrane was on average as high as approximately 131 mg P day^{-1}. The P recovery step reduced this to on average 8 mg P day^{-1} for R100%-P. The loss of P via the NF permeate was also lower in R100%-P with a value of 10 ± 5 mg P day^{-1} compared with a value of 14 ± 5 mg P day^{-1} for R100%. The proposed use of MBR NF combined with P recovery thus provides the opportunity to produce high quality reusable water, while the occurrence of scaling is significantly reduced.

We also investigated the loss of P via the waste sludge of the MBRs. Sludge digestion followed by ICP-OES analysis of sludge samples taken on seven different days gave average P concentrations of 18 ± 4, 16 ± 3 and 17 ± 4 mg P per g TSS from the R100%, R100%-P and R0% reactors, respectively. With average TSS concentrations of 4.2 ± 1.5, 4.4 ± 1.2 and 5.1 ± 1.2 g L^{-1}, and 0.432 L day^{-1} of waste sludge, this means that 33, 31 and 37 mg P day^{-1} were lost via the waste sludge from R100%, R100%-P and R0%, respectively. Together with the P in the liquid phase of the waste sludge, this gives total losses of 36, 34 and 44 mg P day^{-1}, respectively. This shows that loss of P via the waste sludge was lowest in the R100%-P system, i.e. the system with P recovery, which seems logical as the P recovery step reduced the presence of P in the system. An even more effective approach in terms of P recovery efficiency and impact on the MBR, would probably be the recovery of P from the NF concentrate before recirculation to the MBR, rather than from the MBR permeate as the P levels are highest in NF concentrates. However, this very much depends on the P concentration in the wastewater inflow, as high P values in the wastewater result in high P concentrations in the MBR permeate (as in our case), leading to severe scaling on the NF [3].

6.3.3 Membrane resistances

6.3.3.1 NF resistance of MBR permeates

To obtain information on the effect of the P removal step on filterability, the three MBR permeates were compared in separate dead-end filtration experiments with fresh NF270 membranes. MBR permeates were sampled as feed and filtered at a transmembrane pressure of 5 bar. The pH of the three MBR permeates was checked and found equal, as the pH in each of the MBRs was continuously adjusted to 7.3.

The change in resistance in time (reported as concentration factor) was monitored for the three different MBR permeates (Fig. 6.6). In contrast with values presented in Section 6.3.2.1 (Fig. 6.2), R100%-P MBR permeate was sampled before the P recovery step was applied, to allow a fair comparison to the two other permeates of the MBRs operated without P removal.

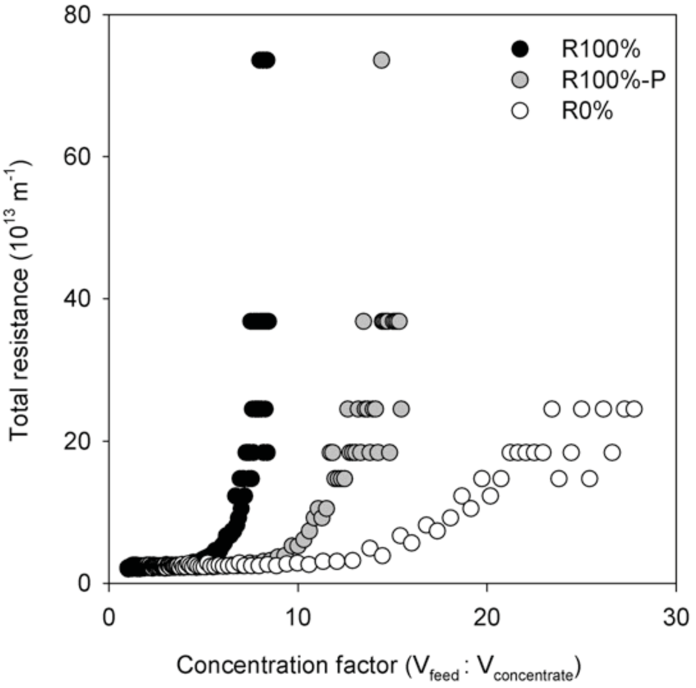

Fig. 6.6. *Total resistance of the MBR permeates in time (reported as concentration factor), filtered in dead-end filtration mode over fresh NF270 membranes at 5 bar.*

Fig. 6.6 shows that the fastest resistance increase occurred with the R100% permeate. The resistance increase in R100%-P was intermediate and the lowest increase was found for the blank. This corresponds well with the P concentrations; the R100% permeate contained 10.3 mg P L^{-1} whereas the R100%-P permeate contained only 6.9 mg P L^{-1} before the P removal step. The R0% permeate contained 6.5 mg P L^{-1}. This confirmed results of our previous research [3], which showed that calcium phosphate scaling dominates NF fouling in this wastewater treatment process.

Rejections of P were 94%, 92% and 96% for R100%, R100%-P and R0%, which is comparable to the rejection of 97 ± 2% found for R100% in the full MBR NF process (Section 6.3.2.2). As mentioned before, the lower P rejection found for the R100%-P permeate is possibly related to more scaling in R100%. The dissolved P concentrations in the NF permeate were 0.6, 0.6 and 0.3 mg L^{-1} for R100%, R100%-P and R0%, respectively; these values are similar to the values found for the full MBR NF process (Fig. 6.4).

In a previous study, NF concentrate recirculation was found to result in higher concentrations of (recalcitrant) organic compounds (TOC) in the MBR permeate [3], which were on average 28 ± 11, 25 ± 11 and 22 ± 16 mg L^{-1} in the R100% and R100%-P and R0%, respectively. This as well may contribute to the higher resistances found with R100%-P permeate than for R0% permeate.

6.3.3.2 Effect of P recovery

The improved filterability of the R100%-P permeate compared with that of R100% (Fig. 6.6) was assumed to be related to the P removal step. To exclude effects that are not directly related to the lower P content, but which could have had an indirect effect, such as a difference in biological performance in the MBR of R100%-P due to the different P concentration in the MBR, we performed additional stirred dead-end filtration tests with the R100% MBR permeate.

In these experiments, P was removed by precipitation at three different pH values and the filterability of these three separate R100% MBR permeate samples was evaluated. We used NaOH to adjust the pH to a value of 8, 9 or 10 to allow different amounts of P to precipitate. After removing the precipitate by centrifugation, the pH of the remaining supernatants was readjusted to 7.3 to exclude effects of pH on filtration of all three batches. Filtration was performed over fresh NF270 membranes. Fig. 6.7 displays the resulting measured resistances.

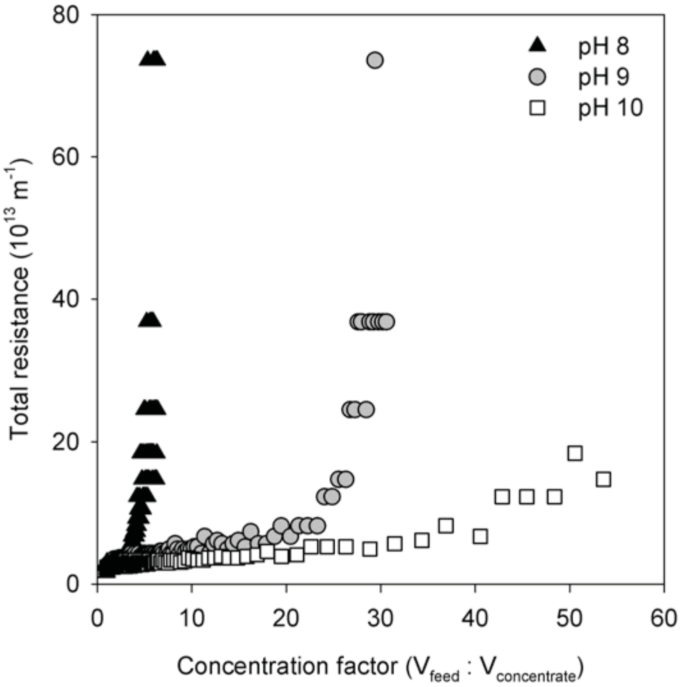

***Fig. 6.7** Total resistance during nanofiltration of three samples of pretreated R100% MBR permeate in time (reported as concentration factor). After P precipitation and removal at different pH 8, 9, or 10, each sample was filtered over fresh NF270 membranes at pH 7.3 in stirred dead-end cells at 5 bar.*

The results clearly show a much stronger resistance increase with concentration factor for the samples treated at lower pH values, i.e. with lower P removal and consequently higher P concentrations in the feed used for NF filtration.

Table 6.2 shows the percentages of P removal after precipitation at different pH values as determined from the difference between the amount of P in the R100% MBR permeate and the three resulting R100% supernatants after precipitation at pH 8, 9 and 10 and centrifugation.

Table 6.2 *Concentrations of calcium, phosphorus and TOC removed from the MBR permeate at different pH values and the corresponding mole ratios of calcium to phosphorus. Value are averages over duplicates of the dead-end filtration tests at different pH.*

	P removed		**Ca removed**		**n (Ca/P)**	**TOC removed**	
	mg L^{-1}	**%**	**mg L^{-1}**	**%**	**-**	**mg L^{-1}**	**%**
pH 8	0.3 ± 0.1	3 ± 2	1.1 ± 0.0	1 ± 0.5	2.6 ± 0.7	0.9 ± 0.2	1 ± 1
pH 9	7.8 ± 2.8	58 ± 3	14.9 ± 4.5	20 ± 6	1.5 ± 0.1	2.7 ± 0.7	10 ± 2
pH 10	11.7 ± 8.2	87 ± 6	22.7 ± 8.2	30 ± 10	1.5 ± 0.0	3.3 ± 1.2	13 ± 5

Especially at higher pH values, a large amount of P was removed. Along with P, also Ca was removed and the molar calcium to phosphorous ratio significantly decreased above pH 8. Also the TOC removal was more efficient at higher pH. This indicates that P most likely precipitated as calcium phosphates, as was also found for the continuous MBR NF experiments (Section 6.3.2.3), though the molar calcium to P ratio was markedly higher at pH 8 when hardly any precipitation occurred. The percentages of the co-precipitated TOC are low relative to the removed Ca and P percentages, which indicate that the precipitate consisted mostly of inorganics with organic that were co-precipitated and were possibly the reason for the amorphous state. The co-precipitated TOC is, at least to a certain extent, in the form of humic acids [3].

Altogether, these batch experiments confirm our earlier hypothesis and suggest that the lower (delayed) NF resistance increase with increasing concentration for R100%-P relative to R100% (Fig. 6.6) is indeed related to the lower P content in the NF feed.

6.4 Conclusions

Treatment of MBR permeate with NF produces high-quality reusable water, but also concentrated waste. In addition, P induced scaling on the NF membrane is a major concern. The work presented in this paper, showed that NF concentrate recirculation combined with P removal from the MBR permeate before the NF, allows the production of reusable water, while at the same time significantly reducing scaling and preventing the production of a highly concentrated waste stream. P removal is the major reason for the improved filterability. In addition, the concept allows the recovery of highly valuable P. P is mostly recovered as inorganics (calcium phosphates).

In such an integrated MBR NF process with concentrate recirculation and additional P removal, P is effectively removed down to a value below 1-2 mg P L^{-1}, which meets the discharge limit and also brings reuse as for example cooling water in power plants within reach.

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7

General Conclusions & Outlook

Abstract

This research on an integrated MBR NF concept with NF concentrate recirculation for wastewater treatment provides details on the operation of such a system, with special focus on the membrane and biological operation. A favorable decrease in sludge production was found, which was however accompanied by the main bottleneck of the system: the membrane operation. Calcium phosphate scaling was found on the NF membrane and in the MBR sludge which did significantly reduce especially the NF operation. Also in the MBR, despite the improved bioflocculation due to NF concentrate recirculation (which did not aid the filterability), the membrane operation was a major issue. Increased organics in the supernatant increased the TMP with concentrate recirculation. A significant operational improvement was made by introducing a phosphorous recovery step into the recirculation loop. This tackled the major bottleneck and improved significantly the membrane operation, especially of the NF. Overall, this combined concept reduces the discharge of a potentially hazardous waste stream to the environment and at the same time helps to recover valuable phosphorous, besides its main aim: the production of reusable water.

7.1 General conclusions

This thesis evaluates and discusses an integrated membrane bioreactor (MBR) and nanofiltration (NF) recirculation concept with the main aim of producing reusable water. The recirculation of the NF concentrate to the MBR minimizes unwanted discharge of a concentrated waste stream. The MBR NF system is evaluated in terms of reduction of conventional wastewater parameters, but also in more detail for biological and membrane performance, quality of NF permeate for water reuse as well as potential for recovery of valuable phosphorous. The results highlight the advantages and challenges of this integrated concept, from a technological, biological and environmental perspective.

Following a general introduction, **Chapter 2** gives an overview of the most important literature contributing to the research on MBR NF processes. The advantages and challenges of the MBR NF recirculation system found in literature were highlighted. The general performance of the MBR NF systems was discussed and also e.g. the interplay between membrane, feed components and solution matrix properties was presented. An extensive contribution in research was found to be related to micropollutants removal. In that case, NF was used to remove especially those micropollutants that pass the MBR with the aim to produce reusable water. Additionally, membrane cleaning strategies were summarized. Before this thesis, only few research papers on the application of NF concentrate recirculation in an MBR NF concept were published. The research described in this thesis continued this work and gives more detailed insight into the challenges and opportunities of such an MBR NF concept.

In the following **Chapter 3** the main focus was on the feasibility of NF concentrate recirculation. The focus in this chapter was predominantly on the biology. The effect of concentrate recirculation was evaluated by comparing two reactor systems; one blank MBR without concentrate recirculation and one MBR with a subsequent NF stage for full NF concentrate recirculation. Focus of the biological performance was a COD mass balance of both reactor systems as well as the sludge production in the MBRs. It was found that the NF concentrate recirculation led to lower sludge production as well as increased mineralization (characterized as the deficit in the COD mass balance). Subsequently, the potential toxicity due to elevated levels of heavy metal concentrations, caused by the NF concentrate recirculation, was discussed. Finally, considering sludge performance, the results showed that NF concentrate recirculation did not dramatically impact the sludge performance, though it cannot be excluded that changes in the bacterial metabolism occurred, which could impact the operation on a longer term.

In contrast to Chapter 3, which focuses on the effect of the biological performance after concentrate recirculation, **Chapter 4** highlights the effect of concentrate recirculation in relation to membrane performance of the MBR and NF. A full recirculation system was compared to a blank MBR reactor. The NF270, selected as the most suitable NF membrane, was applied in the lab scale recirculation system. NF concentrate recirculation resulted in increased ion and organics concentrations in the recirculation system. It was revealed in an early stage NF autopsy that predominantly calcium phosphate scaling occurred. Related to that, a comparison of the NF fouling potential of the two MBR permeates showed increased NF resistance with concentrate recirculation. Both, organics and inorganics in the MBR permeate were increased, though inorganics had a much greater contribution to the higher NF resistances than organics. Therefore, recovery of phosphorous before the NF was suggested to ease the NF operation. NF concentrate recirculation led to a steep increase in transmembrane pressure in the MBR with NF, indicating more severe fouling compared to the blank MBR. The MBR supernatant contributed mostly to the increased TMP compared to the sludge solids only. MBR membrane fouling was therefore attributed to increased colloidal and dissolved COD concentrations in the supernatant.

The possibility to recover phosphorous electrochemically from the NF concentrate was addressed in **Chapter 5.** In such an electrochemical system, NF concentrate is fed to the cathode. The anode and cathode compartment are separated by a cation exchange membrane. A high pH environment is created at the cathode of the electrochemical cell, while an acidic environment is produced at the anode due to water splitting by an electrical potential. The high pH at the cathode led to precipitation of phosphorous as amorphous calcium phosphates and amorphous calcium carbonates in the NF concentrate. The amorphous state of the precipitation originates from the presence of magnesium or humic acids in the NF concentrate. This system could potentially be applied in a continuous sequence such that it can be integrated into the MBR NF concept. In such a continuous sequence, the concentrate is first introduced into the anode compartment to strip the carbonates at low pH and potentially receive a cleaner product in the following precipitation step at the cathode at high pH. Subsequently, the concentrate flows from the anode to the cathode compartment, where precipitation of phosphorous occurs at high pH, finally resulting in a cleaner product (water).

The last chapter (**Chapter 6)** describes the integration of a phosphorous recovery step in the MBR NF process (Chapter 5). Phosphorous was directly removed from the MBR permeate prior to the NF, due to the relatively high calcium and phosphorous contents in the wastewater. These high concentrations cause severe scaling on the NF (Chapter 4). Three reactors were compared: the full recirculation system, the blank MBR without NF, and a full MBR NF recirculation system with phosphorous precipitation in the MBR permeate by NaOH addition. Base addition reached phosphorous removal up to 75%, lowering the phosphorous content in the entire recirculation loop. Calcium and phosphorous were found in the precipitates but also organics and carbonates. Improved NF operation was found for the system with concentrate recirculation and phosphorous removal. Phosphorous removal decreased the NF resistance and facilitated the operation. Nevertheless, the blank reactor without concentrate recirculation still showed the best performance in terms of resistance. Besides phosphorous also concentrations of organics but also other inorganics such as magnesium and carbonates were elevated in the loop by the NF concentrate recirculation. Even if phosphorous was removed, these compounds most likely still contributed to the flux decline.

7.2 Outlook

The MBR NF concept allowed the production of reusable water (NF permeate), while at the same time reducing the amount of concentrated waste and recovering valuable components (e.g. phosphorous). Some opportunities for future research remain after this thesis:

7.2.1 Sludge reduction and sludge treatment

The NF concentrate recirculation, as proposed in this work, leads to decreased sludge production. This is economically beneficial as lower sludge production decreases the costs for waste sludge disposal. Several methodologies to reduce sludge production and with that costs for sludge treatment are discussed in literature [1, 2]. A mechanism related to this is called “uncoupling”. With the energy gained from substrate mineralization to carbon dioxide, the bacteria can produce biomass. However, due to an uncoupling of catabolism and anabolism, only lower amounts of energy are available for this biomass growth. Instead, more energy is needed for instance for cell maintenance. This uncoupling can be caused by organic protonophores or heavy metals [1] but also natural organic matter such as humic or fulvic acids. Especially hydrophobic weak acids groups, also present in natural organic matter [3], were identified as potential uncouplers in literature [4].

Based on this research it was not possible to identify the reason for the lower sludge production in this MBR NF concept. It has to be further investigated whether reduced sludge production in the case of NF concentrate recirculation is connected to lower mineralization and therefore to uncoupling or if other mechanisms such as cell lysis or presence of hydrolysis enzymes are important. More specifically, identification of this possible uncoupling mechanism and the compounds causing this should be performed in the future.

So far, the specific effect of NF concentrate recirculation on sludge treatment such as anaerobic digestion, dewatering and sludge incineration is also not known yet. Literature states that increased cation concentrations improve the dewaterability [5]. Anaerobic digestion could be impacted by inorganics precipitation as this is suggested to limit mass transfer and with that decreases the biological activity [6]. Also increased heavy metal concentrations in the sludge can be expected due to concentrate recirculation. The maximum allowable values are imposed by regulations of the European community [7]. For instance, copper is restricted to 1,000-1,750 mg kg^{-1} of dry matter for sludge application in agriculture, while the sludge of the recirculation system produced in this research exceeds 2,000 mg kg^{-1}. This simply shows that sludge treatment requires specific attention, depending on the disposal route selected.

7.2.2 Membrane operation and fouling

A reduction in scaling caused by calcium phosphates is achieved by implementing a phosphorous recovery step. Nevertheless, the operation of the membranes within this MBR NF concept remains a challenge. Specifically dissolved compounds like humic acids can be a reason for flux decline, which in the MBR is related to the supernatant [8]. As NF concentrate recirculation increases the concentration of these components in the MBR as well, those may cause additional flux decline.

Therefore, possible improvements in terms of fouling should not only be related to the type of membrane itself but also to the specific configuration used in the MBR operation. The use of hollow fibers for instance enables membrane backwashing, which offers an additional method to control fouling besides the commonly applied relaxation steps [9, 10]. It is still questionable whether this would help to solve fouling by dissolved material related to adsorption rather than cake formation. Additionally, for example, the use of UF membranes instead of MF membranes in the MBR will improve the rejection of dissolved organics. As such, this will decrease fouling on the NF membrane, but may lead to increased fouling on the MBR membranes [11]. Generally, side-stream MBR configurations, such as the PentAir (formerly NORIT) AirLift MBR [12], also contribute to fouling control as this system makes cleaning in place possible [13]. Membrane fouling by dissolved organics can be tackled by additional concentrate treatment such as oxidation by ozone and UV or adsorption on activated carbon [14].

7.2.3 Calcium phosphates – dissolution and separation

The continuous process presented in the outlook of Chapter 5 is a basis for continuous phosphorous recovery in a side stream of the MBR NF system. It remains questionable how well the separation of the phosphorous precipitates can be performed in a larger scale system. The separation of an amorphous phase from the water is not always trivial and might need additional effort depending on the throughput. If batchwise or slow separation of the phosphorous product is possible, separation can simply be achieved by conventional settling. If however higher throughput is necessary also centrifuges, filtration or addition of seed material can be applied. The occurrence of phosphorous precipitation is very dependent on the specific wastewater composition. Additionally also the dissolution rates of the precipitated amorphous calcium phosphates have to be investigated to decide about their applicability for instance as a fertilizer. For fertilizer applications, especially biological and elemental contamination are of great concern when wastewater is the origin of the product [15]. One issue with all wastewater applications is the incorporation of heavy metals as well as organics into the final product. Additional treatment (e.g. ion exchange) might be needed to increase the purity of the precipitates.

7.2.4 Micropollutant removal

Also micropollutants can be removed by the MBR NF recirculation process. As the majority of the micropollutants is retained by the NF membrane, many researchers only use the MBR permeate matrix and spike this with micropollutants to perform NF rejection experiments [16-19]. However, this only gives partial insight in the removal capacity of such an MBR NF system, as also the MBR may contribute to the overall rejection. Especially, more research should be performed on whether NF concentrate recirculation increases the removal capacity of the MBR NF concept.

On the other hand, also some micropollutants are known to be difficult to address and remove by the MBR NF process, such as caffeine [20], carbamazepine [19, 21] or acetaminophen [22]. In these cases, other types of NF membranes have to be investigated or the use of RO membranes has to be considered, especially when those components are of great concern.

7.3 Further opportunities

The NF concentrate recirculation investigated in this work most dominantly interfered with the MBR membrane operation rather than the biological operation. For future applications of this full NF concentrate recirculation concept the presence of the phosphorous recovery step is very important. Therefore, especially the selection of a suitable separation mechanism for phosphates needs to be found. A finalized concept with concentrate recirculation, phosphorous recovery as well as separation and potential degradation of micropollutants could make this process highly valuable for reusable water production.

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Summary

Summary

Increasing water shortages drive the need for sustainable water treatment and especially the reuse of water. Membrane technology is very suitable for the treatment and purification of wastewater. Permeate resulting from secondary wastewater treatment using a membrane bioreactor (MBR) can be followed by nanofiltration (NF) for tertiary polishing, allowing the production of high quality water. The produced NF concentrate is a potential environmental hazard, which nevertheless is often discharged in the environment. To decrease this environmental impact of wastewater treatment, it is suggested to recirculate the NF concentrate back to the MBR reactor. Additionally, the production of more concentrated waste streams allows the recovery of valuable components (e.g. minerals) from the waste streams.

In this thesis, the impact of NF concentrate recirculation and the recovery of phosphorous on an MBR process for the treatment of wastewater are considered. In more detail, especially the impact of concentrate recirculation on the biology in the MBR, as well as the MBR and NF membrane performance are assessed. The possibility to recover valuable phosphorous electrochemically, but also the implementation of a phosphorous recovery step into such a continuous MBR NF system are presented.

Following the general introduction, **Chapter 2** gives a summary of the current literature on MBR NF processes. After highlighting the factors that impact the MBR NF operation, a literature overview of the performances and capabilities of these MBR NF systems is presented. Special emphasis is given to micropollutant removal, and literature suggests that MBR and NF have a great potential to remove micropollutants to a large extent. Despite that, some persistent micropollutants are hard to remove either in the MBR or in the NF and might have to be tackled by other treatments such as reverse osmosis (RO). Several cleaning strategies for MBR as well as NF are summarized. Only few papers specifically focusing on NF concentrate recirculation are found, and the influence of this recirculation on the process is highlighted. Biodegradation was found to be enhanced and impacts on nitrification were not found. NF concentrate recirculation in MBR NF processes was mostly considered when highly polluted streams, containing recalcitrant organic compounds, had to be treated. Additional treatment steps (mostly treating those accumulated organics) such as oxidation or adsorption were often required, which are also summarized in this chapter.

Chapter 3 investigates the consequences of NF concentrate recirculation to the MBR for the microbiology in an MBR NF process. A comparison of the results with a reference MBR without concentrate recirculation indicates that the biological performance (COD removal and nitrification) of the MBR is not drastically affected by concentrate recirculation. No improvement in biodegradation was found. The NF concentrate reduces the sludge production by 21% and with that also the sludge disposal costs. Recirculation improves the quality of the sludge flocs in terms of compactness and settleability (shear stress). A main drawback of the concentrate recirculation is the increased fouling of the MBR membranes with recirculation, compared to the reference MBR without. Recirculation of non-biodegradable (soluble) organics is found to be a major issue regarding MBR fouling.

Chapter 4 highlights specifically the impact on membrane operation of both the MBR as well as the NF membranes in an MBR NF process with NF concentrate recirculation. A long-term investigation (1 year) showed that the NF permeate quality is not impacted by the recirculation, which shows the potential of the process for reusable water production. Fouling of the MBR membranes was observed and is caused by the MBR supernatant due to colloidal and dissolved organics. Consequently more frequent membrane cleaning is required for the recirculation reactor. Also NF membrane fouling was observed and mostly consists of inorganics (calcium and phosphate), while organics (e.g. humic acids) do not have a major impact on the NF fouling. In fact, the elevated concentrations of humic acids even enhance the flux of the NF.

Simultaneous phosphorous recovery from the NF concentrate recirculation in an MBR NF process has the potential to decrease NF scaling. An electrochemical system to recover phosphorous is presented in **Chapter 5**, using an electrochemical cell divided into an anode and a cathode compartment separated by a cation exchange membrane. The precipitation of phosphorous is performed using real nanofiltration concentrate by locally increasing the pH at the cathode surface due to water electrolysis creating supersaturated conditions. 70 - 95% of total orthophosphate is recovered (at pH 8 - 10). Further analysis by ICP, XRD and ATR-FTIR indicates the presence of amorphous calcium phosphate (ACP). Depending on the pH also minor parts of amorphous calcium carbonate (ACC) are precipitated. Performance losses of the electrochemical system for instance by scaling at the cathode surface are not found. Scaling possibly is prevented by H_2-gas formation at the cathode.

Nutrient (phosphorous) recovery implemented in an integrated MBR NF process with NF concentrate recirculation is discussed in **Chapter 6**. This chapter shows the performance of two laboratory-scale MBR NF processes with NF concentrate recirculation, one with and one without P recovery from the MBR permeate, operated for 200 days. The experiments also include a third “blank” MBR, neither with NF concentrate recirculation nor P recovery. The recovery step results in NF permeate with a sufficiently low P level that allows discharge or reuse as for instance cooling water in power plants. P recovery significantly improves the filterability (decrease of the NF filtration resistance) of the MBR permeate. Scaling especially on the NF membrane is reduced by the addition of the P recovery step.

To conclude this thesis, **Chapter 7** gives an outlook for future research on this integrated MBR NF membrane concept with concentrate recirculation and nutrient recovery. The process produces high quality, reusable water as the NF permeate, and at the same time reduces the amount of concentrated waste and even allows the recovery of valuable (e.g. phosphorous) components. Nevertheless, the use of two membrane systems can be energy and especially maintenance intensive. Also, the decreased sludge production and increased membrane fouling raise some challenges. More research regarding additional sludge treatment facilities, the use of different membrane types and configurations as well as the quality and separation of the obtained calcium phosphates is suggested. Although not experimentally investigated in this thesis, the concept is very attractive for micropollutant removal and more detailed research on the behavior of specific emerging micropollutants in the MBR NF process with concentrate recirculation is important.

Samenvatting

Samenvatting

Toenemende watertekorten doen de noodzaak tot duurzame waterbehandeling en vooral het hergebruik van water toenemen. Membraantechnologie is zeer geschikt voor de behandeling en zuivering van afvalwater. Permeaat van een secundaire afvalwaterbehandeling waarin een membraan bioreactor (MBR) wordt gebruikt, kan verder worden behandeld door middel van nanofiltratie (NF) voor een tertiaire zuivering. Dit maakt het mogelijk water van hoge kwaliteit te produceren. Het geproduceerde NF-concentraat vormt weliswaar een potentieel gevaar voor het milieu, maar wordt toch vaak geloosd. Om dit schadelijke effect van afvalwaterbehandeling op het milieu te minimaliseren, is voorgesteld het NF-concentraat te recirculeren terug naar de MBR-reactor. Dit resulteert tevens in de productie van sterker geconcentreerde afvalwaterstromen, wat de terugwinning van waardevolle componenten (b.v. mineralen) uit de afvalwaterstroom mogelijk maakt.

In dit proefschrift wordt het effect van de recirculatie van NF-concentraat en de terugwinning van fosfor in een gecombineerd MBR NF proces voor de behandeling van afvalwater onderzocht. Meer specifiek wordt gekeken naar de invloed van concentraatrecirculatie op zowel de biologie in de MBR alsook op de prestaties van de MBR en het NF-membraan. Daarnaast worden de mogelijkheid om waardevol fosfor elektrochemisch terug te winnen en de implementatie van een fosforterugwinningsstap in een continu MBR NF proces gepresenteerd.

Na de algemene inleiding geeft **Hoofdstuk 2** een samenvatting van de huidige literatuur over MBR NF processen. Na beschrijving van de factoren die invloed hebben op de werking van MBR NF systemen, wordt op basis van de literatuur een overzicht van de prestaties en de toepasbaarheid van deze systemen gepresenteerd. De nadruk ligt daarbij op de verwijdering van microverontreinigingen. De literatuur laat zien dat het MBR NF concept in potentie een zeer aantrekkelijke methode is om dergelijke verontreinigingen te verwijderen. Desondanks zijn sommige hardnekkige verontreinigingen moeilijk te verwijderen in de MBR of met NF en moeten deze worden aangepakt door middel van andere behandelingen zoals omgekeerde osmose (RO). Verscheidene reinigingsstrategieën voor zowel de MBR als het NF membraan worden samengevat. Slechts een klein aantal artikelen besteedt specifieke aandacht aan NF-concentraatrecirculatie en de invloed van deze recirculatie op het proces wordt besproken. De beperkt beschikbare literatuur laat zien dat in een gecombineerd MBR NF proces biodegradatie versterkt wordt, terwijl de invloed op de nitrificatie zeer beperkt is. De literatuur laat zien dat NF-concentraatrecirculatie in MBR NF processen vooral wordt overwogen wanneer sterk vervuilde stromen die recalcitrante organische stoffen bevatten,

behandeld moeten worden. Additionele behandelingsstappen zoals oxidatie of adsorptie blijken vaak nodig voor verdere behandeling en verwijdering van deze geaccumuleerde organische stoffen.

Hoofdstuk 3 onderzoekt de consequenties van NF-concentraatrecirculatie naar de MBR op de microbiologie in een MBR NF proces. Een vergelijking van de resultaten met een referentie-MBR zonder concentraatrecirculatie laat zien dat de biologische prestatie (CZV-verwijdering en nitrificatie) van de MBR niet drastisch wordt beïnvloed door concentraatrecirculatie. Er is geen verbetering in biodegradatie gevonden. Het NF-concentraat reduceert de slibproductie met 21% en daarmee ook de verwijderingskosten van het slib.
Recirculatie verbetert de kwaliteit van de slibvlokken wat betreft compactheid en bezinking. Een nadeel van concentraatrecirculatie is echter de toegenomen vervuiling van de MBR-membranen in vergelijking met de referentie-MBR. Recirculatie van niet-biologisch afbreekbare (oplosbare) organische componenten is een is een belangrijke reden voor MBR-vervuiling.

Hoofdstuk 4 licht specifiek de invloed van NF-concentraatrecirculatie op de operatie van zowel de MBR als NF membranen in een gecombineerd MBR NF process toe. Een langeduur onderzoek (1 jaar) laat zien dat de kwaliteit van het NF-permeaat niet wordt beïnvloed door de recirculatie, hetgeen de potentie van het proces voor de productie van herbruikbaar water aantoont. Vervuiling van de MBR-membranen werd waargenomen en is te wijten aan colloïdale en opgeloste organische stoffen. Om de vervuiling beheersbaar te houden is meer frequente reiniging van het membraan noodzakelijk voor het systeem met NF concentraatrecirculatie. Ook vervuiling van het NF membraan werd waargenomen en deze bestond vooral uit anorganische stoffen (calcium en fosfaat), terwijl organische stoffen (b.v. humuszuren) geen grote invloed hebben op de NF-vervuiling. De verhoogde concentraties van humuszuren verhoogde zelfs de flux van de NF.

Gelijktijdige fosforterugwinning uit de NF-concentraatrecirculatiestroom in een MBR NF process heeft de potentie om anorganische vervuiling van het NF membraan te verminderen. In **Hoofdstuk 5** wordt een elektrochemisch systeem voor de terugwinning van fosfor gepresenteerd, waarin een elektrochemische cel verdeeld in een anode- en kathodecompartiment gescheiden door een kationuitwisselingsmembraan wordt gebruikt. De precipitatie van fosfor wordt geïnduceerd door lokaal aan het kathodeoppervlak de pH te verhogen door middel van de elektrolyse van water, wat oververzadigde condities creëert. De resultaten laten zien dat met natuurlijk afvalwater 70-95% van het totale orthofosfaat wordt teruggewonnen (bij pH 8-10). Verdere analyse met behulp van ICP, XRD en ATR-FTIR laat de vorming van amorf calciumfosfaat (ACP) zien. Afhankelijk van de pH precipiteren ook kleinere hoeveelheden amorf calciumcarbonaat (ACC). Prestatieverlies van het elektrochemische systeem, door bijvoorbeeld scaling op het kathodeoppervlak, werd niet waargenomen. Scaling wordt mogelijk voorkomen door de vorming van gasormig H_2 aan de kathode.

De werking van een volledig geïntegreerd MBR NF process met NF-concentraatrecirculatie en de terugwinning van fosofor wordt besproken in **Hoofdstuk 6**. In dit hoofdstuk worden de prestaties gedurende 200 dagen van twee laboratoriumschaal MBR NF processen met NF concentraatrecirculatie met elkaar vergeleken, één met en één zonder fosforterugwinning uit het MBR-permeaat. De prestaties van deze beide systemen worden vergeleken met een derde MBR waarin noch NF-concentraatrecirculatie noch fosforterugwinning worden toegepast. De terugwinningsstap resulteert in NF-permeaat met een fosforconcentratie die laag genoeg is om lozing mogelijk te maken of voor gebruik als bijvoorbeeld koelwater in energiecentrales. Fosforterugwinning verbetert de filtreerbaarheid van het MBR-permeaat significant (afname van de NF-filtratie weerstand). Ook scaling op met name het NF membraan wordt sterk gereduceerd door fosforterugwinning.

Ter afsluiting van dit proefschrift worden in **Hoofdstuk 7** de belangrijkste conclusies van dit onderzoek samengevat en worden een aantal richtingen voor verder onderzoek aan dit geïntegreerde MBR NF-membraanconcept met concentraatrecirculatie en de terugwinning van waardevolle componenten beschreven. Het proces produceert water van hoge kwaliteit in de vorm van NF-permeaat dat geschikt is voor hergebruik. Daarnaast resulteert het in een vermindering van de hoeveelheid concentraat en maakt het terugwinning van waardevolle componenten (b.v. fosfor) mogelijk. Desalniettemin kan het gebruik van de combinatie van twee membraansystemen (MBR en NF) energie- en vooral onderhoudsintentief zijn. Ook de afgenomen slibproductie en toegenomen membraanvervuiling geven een aantal uitdagingen. Meer onderzoek naar verdere slibbehandelingsmogelijkheden, het gebruik van andere membraantypes en -configuraties en verder onderzoek naar de kwaliteit en zuiverheid van de verkregen calciumfosfaten wordt voorgesteld. Hoewel niet experimenteel onderzocht in dit proefschrift, is het concept zeer aantrekkelijk voor de verwijdering van microvervuiling, maar is meer gedetailleerd onderzoek naar het gedrag van specifieke microvervuiling in het MBR NF-proces met concentraatrecirculatie noodzakelijk.

Zusammenfassung

Zusammenfassung

Der gegenwärtige Anstieg des Verbrauches von Frischwasser und die damit verbundene Wasserknappheit führen zu einem verstärkten Interesse an der Rückgewinnung und Wiederverwendung von Wasser, insbesondere durch nachhaltige und umweltfreundliche Techniken. Membrantechnologien sind besonders geeignet zur Aufbereitung von kommunalen aber auch industriellen Abwässern bis hin zu Reinstwasser. Permeate, welche durch den Einsatz von Membransystemen in der biologischen Stufe der Abwasserbehandlung entstehen (Membranbioreaktor - MBR), können mit Hilfe von Nanofiltration (NF) noch weiter aufgereinigt werden. Dies führt zur Generierung von qualitativ sehr hochwertigem Wasser, nichtsdestotrotz fallen bei der Nanofiltration potenziell umweltgefährdende Konzentrate an, welche oftmals unbehandelt in die Umwelt entsorgt werden. Um dieser potenziellen Umweltgefährdung entgegen zu wirken, wird versucht diese NF Konzentrate innerhalb eines MBR NF Systems unbehandelt in den MBR zurückgeführt. Zusätzlich erlaubt die Produktion von NF Konzentraten jedoch auch die Wiedergewinnung von zum Beispiel wertvollen Nährstoffen (z.B. Phosphate) aus dem so gesehenen konzentrierten Abfall.

In dieser Arbeit wird der Einfluss der Rückführung von unbehandelten NF Konzentraten in den MBR innerhalb der Abwasseraufbereitung und die gleichzeitige elektrochemische Wiedergewinnung von Phosphaten untersucht. Im Detail werden sowohl der Einfluss auf die biologischen Prozesse im MBR als auch die Membranprozesse in MBR und NF präsentiert. Zusätzlich wird die Integration eines Systems zur elektrochemischen Phosphatrückgewinnung in den MBR NF Prozess diskutiert.

Einer allgemeinen Einleitung (**Kapitel 1**), folgend wird in **Kapitel 2** der derzeitige Stand der Literatur im Überblick gegeben. Nach der Diskussion der Einflussfaktoren auf das MBR NF System, werden Leistung und Anwendungsmöglichkeiten eines MBR NF Systems zusammengefasst. Besonderes Augenmerk liegt hierbei auf der hohen Elimination von Spurenschadstoffen mit Hilfe von MBR NF. Dies zeigt jedoch auch, dass zur Entfernung mancher persistenten Spurenschadstoffe andere Prozesse wie zum Beispiel eine Umkehrosmosemembran (RO) benötigt werden. Außerdem werden verschiedenste in MBR NF angewandte Verfahren zur Membranreinigung zusammengefasst. In der Literatur wurde gefunden, dass der biologische Abbau durch die Konzentratrückführung erhöht wurde, die Nitrifikation jedoch nicht beeinflusst wurde. Die Rückführung innerhalb des MBR NF Prozesses wurde speziell bei stark mit organischem Material verunreinigten Abwässern diskutiert. Dies macht die Anwendung zusätzlicher Prozesse zur Unterbindung der

Ansammlung von organischem Material, meist durch oxidative Prozesse oder Absorption, notwendig. Diese additiven Prozesse sind in Kapitel 2 ebenfalls präsentiert.

Kapitel 3 befasst sich mit den Konsequenzen der Rückführung des Konzentrates auf die im MBR befindlichen mikrobiologischen Prozesse der MBR NF Kombination. Der Vergleich mit einem MBR Referenzsystem ohne Konzentratrückführung zeigt, dass die biologische Leistung (CSB Abbau und Nitrifikation) im MBR sich nicht drastisch verändert. Jedoch wurde keine Verbesserung der biologischen Abbaubarkeit festgestellt, wie in der Literatur vereinzelt vermerkt. Das Konzentrat verursacht eine Minderung der Schlammproduktion um 21%, wodurch die Kosten für die finale Abwasserschlammbehandlung verringert werden können. Die Rückführung verbessert die Flockenbildung des Schlammes im Bezug auf Kompaktheit und Absetzbarkeit (Scherbeanspruchung). Die Hauptbeeinträchtigung durch die Konzentratrückführung ist die erhöhte Membranverschmutzung, als Membranverschlammung bezeichnet, im Vergleich zum MBR Referenzsystem ohne Rückführung. Die Rückführung nicht abbaubarer gelöster Stoffe wird als eine der Hauptproblematiken des MBRs festgestellt.

In **Kapitel 4** werden die Einflüsse der Konzentratrückführung auf die MBR und die NF Membranen präsentiert. Ein Langzeitexperiment über die Dauer eines Jahres zeigt, dass die Qualität des NF Permates kaum beeinflusst wurde und dieses ein hohes Potenzial zur Wiederverwendung aufweist. Es wurde beobachtet, dass Membranverschmutzung im MBR hauptsächlich durch gelöstes und kolloidales organisches Material verursacht wird. Im Vergleich zum Referenzsystem ohne Konzentratrückführung werden im Reaktor mit Konzentratrückführung vermehrt Reinigungsprozesse benötigt. Ebenfalls in der Nanofiltration werden aufgrund der Konzentratrückführung vermehrt anorganische meist calcium- und phosphathaltige Ausfällungen beobachtet. Organische Verschmutzungen (z.B. Huminstoffe) haben jedoch keinen größeren Einfluss auf die Leistung der Nanofiltration. Tatsächlich führen gesteigerte Konzentrationen an Huminstoffen sogar zur Erhöhung der Durchflussmenge.

Die erwähnte simultane Wiedergewinnung von Phosphaten aus dem NF Konzentrat während der Konzentratrückführung können eben diese anorganischen Ausfällungen auf der NF Membran verringern. Ein elektrochemisches System zur Phosphatrückgewinnung wird in **Kapitel 5** präsentiert. Hier wird eine elektrochemische Zelle mit Hilfe einer Kationaustauschmembran in einen Anoden- und einen Kathodenbereich geteilt. Die Ausfällung von Phosphor aus Nanofiltrationskonzentraten wird durch die lokale Erhöhung des pH Wertes im Kathodenbereich erreicht. Dies geschieht durch die Aufspaltung von Wasser mittels Elektrolyse, durch welche eine Sättigung im Kathodenbereich entstehen. 70-

95% des Orthophosphates können so bei pH 8 - 10 wiedergewonnen werden. Weitere Analysen des ausgefällten Materials mittels ICP, XRD und ATR-FTIR (Inductively coupled plasma, X-ray diffraction and attenuated total reflectance - Fourier transform infrared spectroscopy) zeigen die Präsenz von amorphem Kalziumphosphat (amorphous calcium phosphates, ACP). Je nach pH Wert sind auch kleinere Mengen von amorphem Kalziumcarbonat (amorphous calcium carbonate, ACC) ausgefällt. Eine Minderung der Leistung des elektrochemischen Systems aufgrund von Ablagerungen auf der Kationenaustauschmembran wurde nicht festgestellt. Die Ablagerung wurde vermutlich durch die Bildung von Wasserstoffgas an der Kathode verhindert.

Die Eingliederung der Wiedergewinnung von Nährstoffen wie zum Beispiel Phosphor in einem MBR NF Prozess wird in **Kapitel 6** erläutert. Hier werden die Ergebnisse dreier im Labormaßstab durchgeführte MBR NF Prozesse über eine Zeit von 200 Tagen präsentiert. Zwei dieser drei Prozesse laufen mit Konzentratrückführung und einer davon beinhaltet zusätzlich einen Phosphatwiedergewinnungsprozess, welcher nach dem MBR integriert ist. Der dritte Reaktor dient als Referenzsystem ohne Konzentratrückführung oder Phosphatwiedergewinnung. Im System mit Konzentratrückführung können mittels der Phosphatrückgewinnungsstufe niedrige Konzentrationen erreicht werden, die ausreichen um Wasser für zum Beispiel Kühlsysteme in Kraftwerken zu liefern. Die Wiedergewinnung von Phosphor erhöht die Filtrierbarkeit durch die Verringerung des Filtrationswiderstandes des MBR Permeates. Anorganische Ablagerungen auf der NF Membran wurden zusätzlich durch die Phosphatwiedergewinnung reduziert.

Abschließend wird in **Kapitel 7** eine Zusammenfassung gegeben in der zukünftige Experimente mit einem MBR NF Prozess mit NF Konzentratrückführung und Nährstoffwiedergewinnung präsentiert werden. Der Prozess liefert durch das NF Permeat qualitativ reines Wasser, welches zur Wiederverwendung genutzt werden kann. Trotz alledem entstehen gleichzeitig hoch konzentrierte Abfälle (Konzentrate), die zwar einerseits eine Rückgewinnung von wiederverwertbaren Nährstoffen erlauben, andererseits allerdings können Membranprozesse energie- und wartungsintensiv sein. Die verringerte Produktion von Schlamm und die erhöhte Membranverschmutzung bieten einige Herausforderungen. Weitere Forschung in den Bereichen der Schlammbehandlung, der Verwendung verschiedenster Membransorten in diesem System und Nutzung anderer Membrankonfigurationen sollte erfolgen. Auch die Effizienz der Trennung der amorphen Calciumphosphate bleibt fraglich. Das MBR NF System kann auch ein attraktives Konzept zur Eliminierung von Spurenschadstoffen sein. Detaillierte Forschung zum Verhalten von Spurenschadstoffen in einem MBR NF System mit Konzentratrückführung ist zu empfehlen.

About the author

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Christina Kappel, born on the 11th of August in Neuss (Germany), graduated high school in 2004. After considering to study graphic design she decided to start her studies in the field of water and received a B.Sc. degree in “Water Science – Chemistry, Analytics, Microbiology” at the University of Duisburg-Essen (Duisburg, Germany) in 2008. Finishing her bachelor thesis with a project at Thames Water R&D (Reading, United Kingdom) on wastewater treatment, she decided to stay for her master studies in the UK. Christina received the M.Sc. degree on “Water and Wastewater Technology” from Cranfield University (Cranfield, United Kingdom) in 2009 after finishing her M.Sc. project at Thames Water R&D (Reading, United Kingdom). In 2009 Christina started working at Wetsus (Leeuwarden, The Netherlands) on her PhD topic “An integrated membrane bioreactor – nanofiltration concept with concentrate recirculation for wastewater treatment and nutrient recovery” with the University of Twente (The Netherlands), until today.

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