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ENHANCED MICROPOLLUTANT REMOVAL AND NUTRIENT RECOVERY IN MUNICIPAL WASTEWATER TREATMENT

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Abstract

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Depleting natural resources such as fresh water and phosphate minerals creates pressure to pursue towards resource recovery in municipal wastewater treatment. In addition, the aquatic environment is under stress due to eutrophication as well as increasing presence of harmful micropollutants, such as pharmaceuticals, hormones and pesticides. Traditional municipal wastewater treatment is not designed for micropollutant removal and treatment plants also struggle with tightening discharge limits. Advanced technologies are required to tackle these challenges.

This thesis examines advanced wastewater treatment technologies for enhanced micropollutant removal and nutrient recovery by focusing on technologies that minimize the use of chemicals. Nanofiltration, reverse osmosis, electrodialysis and pulsed corona discharge oxidation studied gave promising results concerning micropollutant removal. For instance, >90% removal of target pollutants diclofenac, carbamazepine and furosemide could be obtained. Oxidation degraded all target pollutants below 0.1 µg/L with only 0.2 kWh/m^3 oxidation energy when MBR permeate was treated. Oxidation was identified as the most promising technology when only pollutant degradation from MBR permeate is required. However, nanofiltration could be suitable in applications where enhanced micropollutant removal as well as COD, DOC and phosphorus is required.

Size exclusion, hydrophilicity and electrostatic interactions were the main micropollutant removal mechanisms in nanofiltration, whereas size exclusion was the key factor in reverse osmosis. The molecular weight, the amount of double bonds within the molecule and $\cdot$OH degradation constant were the main parameters for pollutant degradation in oxidations according to regression analyses. Molecule hydrophilicity and electrostatic interactions had the strongest influence for pollutant transport in electrodialysis. Overall, the micropollutant removal in the studied technologies appeared to be a combination of several pollutant properties, water matrix and process specific conditions.

Two-stage nanofiltration process coupled with phosphorus precipitation was able to minimize the amount of membrane concentrate by reaching a final VRF value of 300 with minor membrane fouling whilst calcium phosphate was spontaneously precipitated with a 52% recovery rate. Pilot scale electrodialysis produced a highly concentrated fertiliser product rich in NH$_4^+$-N (7.1 g/L) and K$^+$ (2.5 g/L) by concentrating nutrient ions from centrate wastewater with a low energy consumption of 4.9 kWh/kg NH$_4^+$-N. The studied processes could help to guarantee a safer aquatic environment for future generations.

Keywords: electrodialysis, micropollutant removal, nanofiltration, nutrient recovery, pulsed corona discharge, shear enhanced membrane filtration

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Finally, I owe my deepest gratitude and love to my dear wife Salla. You are the light of my life and I am pretty sure that this PhD work would have never been completed without your continuous support and understanding. Thanks for bearing with me and for sharing both the greatest and the darkest times with me during this journey.

Now it is time to turn the page and discover what new journey awaits.

Kimmo Arola
March 2020
Espoo, Finland

"Don't be guided by fear or failure
It's now or never
Just give it all in"

Insomnium – Weather The Storm

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List of publications

This thesis is based on the following publications, which are referred in the text by the Roman numerals I–VI. The rights have been granted by publishers to include the material in the dissertation.

I Arola, K., Kallioinen, M., Van der Bruggen, B., Mänttäri, M. 2019. Treatment options for nanofiltration and reverse osmosis concentrates from municipal wastewater treatment: A review, Crit. Rev. Environ. Sci. Technol., 49 (22), 2049–2116.

II Arola, K., Hatakka, H., Mänttäri, M., Kallioinen, M. 2017. Novel process concept alternatives for improved removal of micropollutants in wastewater treatment, Sep. Purif. Technol. 186, 333–341.

III Arola, K., Mänttäri, M., Kallioinen, M. 2020. Two-stage nanofiltration for minimization of concentrate volume and simultaneous recovery of phosphorus in tertiary treatment of municipal wastewater, Revised manuscript under review in Sep. Purif. Technol.

IV Arola, K., Kallioinen, M., Reinikainen, S.-P., Hatakka, H., Mänttäri, M. 2018. Advanced treatment of membrane concentrate with pulsed corona discharge, Sep. Purif. Technol. 198, 121–127.

V Ward, A., J., Arola, K., Mehta, C., M., Batstone, D., J. 2018. Nutrient recovery from wastewater through pilot scale electrodialysis, Water Res., 135, 57–65.

VI Arola, K., Ward, A., J., Mehta, C., M., Batstone, D., J., Mänttäri, M., Kallioinen, M. 2019. Transport of pharmaceuticals during electrodialysis treatment of wastewater, Water Res. 161, 496–504.

Author's contribution

The author was responsible for gathering the literature data and was the main author in the publication I. The author performed most of the experimental work (planning the experiments, conducting experiments and analyses) as well as was the main author in the publications II–IV and VI. In paper V, the author did part of the experimental work as well as wrote the major part of the article together with the co-authors. Analysis chemists and laboratory technicians of the LUT School of Engineering Science (LUT University) and Advanced Water Management Centre (University of Queensland) did part of the analysis work.

Symbols and abbreviations

Symbols

°	Contact angle	–
·OH	Hydroxyl radical	–
K_{biol}	Biological degradation constant	$L/g_{SS}/d$
K_D	Equilibrium dissociation constant, ratio of the concentration of the substance between the solid and aqueous phase at equilibrium conditions	L/kg_{SS}
kO_3	Ozone reaction rate constant	$M^{-1}s^{-1}$
Log K_{OW}	Octanol-water partition coefficient	–
pKa	Acid dissociation constant	–
R2	Coefficient of determination	–
r_s	Spearman's rank correlation factor	–

Abbreviations

AEM	Anion exchange membrane	
AOP	Advanced oxidation process	
BOD_7	Biological oxygen demand, 7 day incubation	mg/L
CAS	Conventional activated sludge process	
CEM	Cation exchange membrane	
COD	Chemical oxygen demand	mg/L
CR	Cross-rotational	
DEET	N,N-diethyl-meta-toluamide	
DO	Dissolved oxygen	mg/L
DOC	Dissolved organic carbon	mg/L
EC	Electrical conductivity	mS/cm
ED	Electrodialysis	
EDS	Energy dispersive X-ray spectroscopy	
E2	17-beta-estradiol	
EE2	17-alpha-ethinylestradiol	
EU	European Union	
GC	Gas chromatography	
H_2SO_4	Sulfuric acid	
HAP	Hydroxyapatite	
HCl	Hydrochloric acid	
HRT	Hydraulic retention time	h
IrMMO	Iridium mixed metal oxide	
LS	Level sensor	
MBR	Membrane bioreactor	
MF	Microfiltration	
MLSS	Mixed liquor suspended solids	g/L

MRM	Multiple reaction monitoring	
MS	Mass spectroscopy	
MSD	Multishift disk system	
MWCO	Molecular weight cut-off value	Da
NaCl	Sodium chloride	
NaOCl	Sodium hypochlorite	
NF	Nanofiltration	
OECD	Organization for Economic Co-operation and Development	
PCD	Pulsed corona discharge	
pps	pulses per second	
PS	Pressure transducer	
PVDF	Polyvinylidene fluoride	
RO	Reverse osmosis	
SEM	Scanning electron microscope	
SRT	Sludge retention time	d
$SUVA_{254}$	Specific UV absorbance at 254 nm	
$Ti/PtIrO_2$	Titanium/platinum iridium oxide	
TMP	Transmembrane pressure	bar
TOC	Total organic carbon	mg/L
TSS	Total suspended solids	mg/L
UF	Ultrafiltration	
UFLC	Ultra-fast liquid chromatography	
UPLC	Ultra-performance liquid chromatography	
VFA	Volatile fatty acids	mg/L
VRF	Volume reduction factor	
VSEP	Vibratory shear enhanced processing technology	

1 Introduction

1.1 Background

Conventional activated sludge processes (CAS) are the most common and traditional processes applied to municipal wastewater. The actual activated sludge is the biomass produced in wastewater by growth of micro-organisms under the presence of dissolved oxygen. The process is called activated because of the high presence of bacteria (filamentous and floc-forming bacteria), protozoa and other micro-organisms in the biomass. In the traditional CAS processes the sewage and activated sludge are mixed together and aerated to add enough oxygen for the biomass to live, grow and multiply in order to breakdown and remove the organic content present in the influent. A traditional process is composed of a water treatment train and sludge train. The water treatment train usually includes a sand, grit and oil removal part as a pre-treatment, often pre-settling, coagulation-flocculation for phosphorus removal and biological treatment (activated sludge) followed by settling/clarification before effluent is discharged. The sludge train normally includes sludge circulation, sludge thickening, dewatering and sometimes further drying before final disposal. CAS processes are designed to remove or to decrease the concentrations bulk organic and inorganic constituent, which could pollute the receiving waters and cause eutrophication. However, these processes are not designed for micropollutant removal and especially the partially biodegradable micropollutants are poorly removed. Many wastewater treatment plants today based on activated sludge processes are struggling with tightening discharge limits for nutrients. (Barceló and Petrovic, 2008; Monsalvo et al., 2014; Papoutsakis et al., 2015; Von Sperling, 2007)

Natural resources such as fresh water and phosphate minerals are depleting at a growing rate. The depleting phosphorus reserves raises concerns about future food production as phosphorus is an essential element to all life and key ingredient in fertilizers to produce high yield crops. The global phosphorus production is expected to peak around 2033 at 29 megatons per year (Fig. 1) after which the production will reduce to a level below 10 megatons by 2100, to a similar level as it was in 1970s (Cordell et al., 2009). At the same

time the demand for food is rapidly increasing due to high population growth, which is set to exceed nine billion by 2050 from the current 7.7 billion in 2019 and reach nearly 11 billion by 2100 (Our World in Data, 2019; UN, 2019). This raises concern on how to guarantee food for the growing population and leads to increasing fertilizer prices due to increased demand for phosphate and nitrogen-based fertilizers, energy costs or resource limitations. Therefore, there is pressure to migrate towards resource recovery and circular economy also in municipal wastewater treatment. Resource recovery in municipal wastewater treatment could be partly implemented by recovering nutrients, such as phosphorus, from municipal wastewater. The European Union has already taken action related to the phosphorus challenge by adding phosphorus to the list of critical raw materials in 2014 and adopting the circular economy action plan in 2016. (Batstone et al., 2015; Cordell et al., 2011; European Commission, 2013; FAO, 2017; Mehta et al., 2015; OECD, 2017; OECD and EU, 2018; Reitzel et al., 2019)
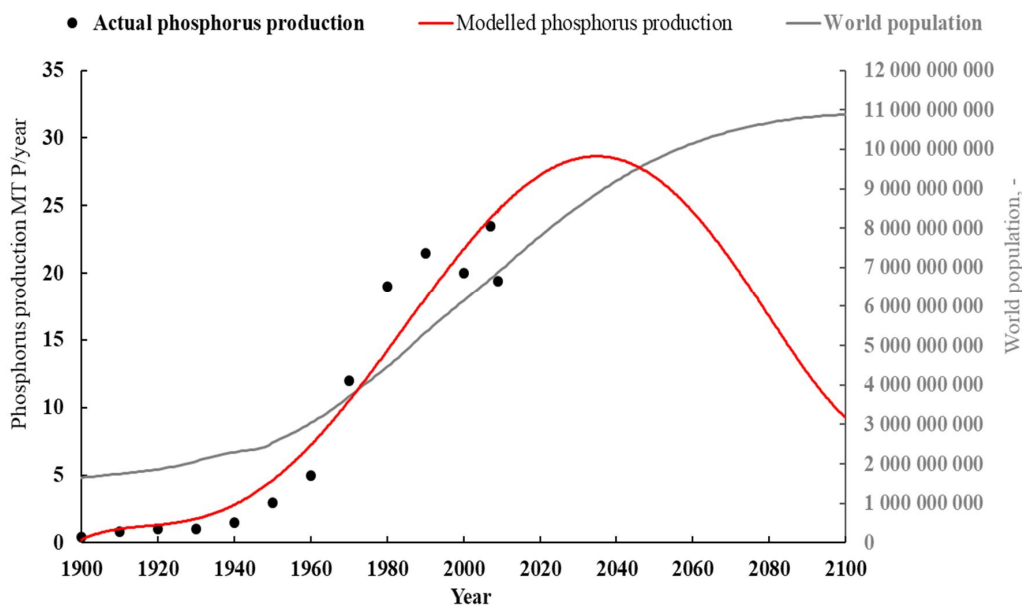

Fig. 1   Indicative peak phosphorus and world population curve. Phosphorus curve illustrates that the global phosphorus reserves are likely to peak around 2033 after which the production of phosphorus will be reduced. Modified and estimated from (Cordell et al., 2009; Our World in Data, 2019; UN, 2019).

Demand for environmental protection is also constantly increasing, which leads to more stringent legislative restrictions on discharges from municipal wastewater treatment plants. Nowadays the aquatic environment is under constant stress due to eutrophication of lakes and other water areas close to sensitive discharge sites of wastewater treatment plants, but also due to increasing presence of harmful micropollutants, such as pharmaceuticals, hormones, pesticides etc., in our aquatic environment. Presence of these micropollutants in nature is a major concern due to their potentially harmful effects on aquatic life such as the hormonal effects for fish. As stated before, many partially biodegradable pharmaceuticals such as diclofenac (non-steroidal anti-inflammatory drug), carbamazepine (anti-depressant) as well as some antibiotics like trimethoprim are not removed efficiently in traditional CAS processes, and therefore these kind of micropollutants are slowly accumulating in nature. (Daughton and Ternes, Thomas, 1999; Daughton and Ruhoy, 2009; Radjenovic et al., 2007; Radjenović et al., 2009; Sipma et al., 2010)

On the other hand, the consumption of pharmaceuticals has significantly increased in the 21st century. According to the Organisation for Economic Co-operation and Development (OECD) the consumption of antihypertensive and antidiabetic drugs has almost doubled in OECD countries between 2000 and 2015, whereas the consumption of cholesterol-lowering drugs has almost quadrupled and the consumption of antidepressant drugs, such as hardly biodegradable carbamazepine, has doubled in OECD countries between 2000 and 2015 as can be seen from the Fig. 2 (OECD, 2017). For instance, in the United Kingdom the daily doses of antidepressants used per 1000 people per day have increased from below 40 doses in 2000 to over 94 doses in 2015. Also in the United States of America the consumption of pharmaceuticals has drastically increased in the recent years, for instance the amount of prescriptions for diclofenac has nearly doubled between 2006 and 2016 (from 5 384 881 to 9 907 530) (ClinCalc, 2019; Sarnak et al., 2017). The fact that many micropollutants such as pharmaceuticals diclofenac, carbamazepine and some antibiotics are not efficiently removed in traditional wastewater treatment and that the consumption of those pharmaceuticals is significantly increasing globally creates great

concerns about the fate of aquatic environment in the future. In addition to aquatic environment also the human health is under concern due to bigger risk for antibiotic resistance as the antibiotic exposure from the environment is increasing. (ClinCalc, 2019; Daughton and Ternes, Thomas, 1999; Daughton and Ruhoy, 2009; OECD, 2017; OECD and EU, 2018; Radjenovic et al., 2007; Radjenović et al., 2009; Sarnak et al., 2017; Sipma et al., 2010)

European Union (EU) has already acknowledged these concerns by setting up a watch list in 2015 containing problematic substances, such as diclofenac, which concentrations should be monitored in surface waters and wastewater treatment plants on a regular basis (European Commission, 2015). However, after revising the 1st watch list in April 2018 the European Commission decided to launch 2nd watch list in June 2018 from where some of the substances, such as diclofenac, has been removed because sufficient amount of good quality monitoring data already exists for some substances (European Commission, 2018; Loos et al., 2018). The 2nd watch list of pollutants to be monitored from the surface waters in the EU contains following substances: hormones 17-alpha-ethinylestradiol (EE2), 17-beta-estradiol (E2) and estrone (E1), macrolide antibiotics erythromycin, clarithromycin and azithromycin, antibiotics amoxicillin and ciprofloxacin, pesticide methiocarb, neonicotinoid insecticides imidacloprid, thiacloprid, thiamethoxam, clothianidin and acetamiprid as well as insecticide metaflumizone (European Commission, 2018).
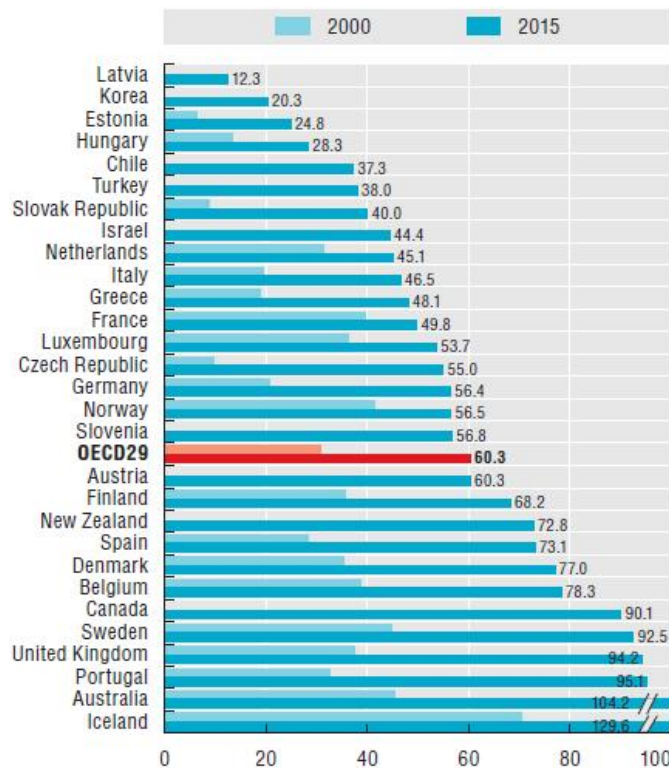
Fig. 2   Antidepressant drugs consumption in OECD29 countries in 2000 and 2015 measured as daily doses per 1000 people per day. (OECD, 2017)

More advanced treatment technologies are required in municipal wastewater treatment in order to tackle the two mega trends of wastewater treatment, micropollutants in wastewaters and resource recovery. By using more efficient technologies the quality of aquatic environment could potentially be significantly improved. This is needed to guarantee safe aquatic environment for the future generations.

1.2   Aim of the study

This study focuses on enhanced nutrient recovery and micropollutant removal in municipal wastewater treatment to tackle some of the current challenges of municipal wastewater treatment. The aim is to examine technologically proven and emerging process solutions for wastewater treatment that will use a minimal amount of chemicals. On this basis nanofiltration and reverse osmosis, which are proven technologies for

tertiary wastewater treatment, as well as emerging technologies electrodialysis and pulsed corona discharge oxidation are selected as main technologies to be researched. Pressure driven membrane technologies, such as nanofiltration and reverse osmosis, concentrates micropollutants and nutrients into membrane concentrate. Therefore, the aim of this study is also to review and conclude the current state of membrane concentrate treatment in municipal wastewater treatment, especially related to value component recovery, such as recovery of phosphorus or ammonium. This topic is addressed in a comprehensive review article.

This PhD study searches answers for following research questions: (1) Are nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED) or pulsed corona discharge (PCD) able to remove over 90% of the target micropollutants of this study, which are present in municipal wastewater treatment effluents, and which of these technologies are the most suitable for this purpose, (2) What are the separation mechanisms for the removal of examined target micropollutants with the utilized technologies and is it possible to predict the micropollutant removal efficiency with the studied technologies based on the target micropollutant properties, and (3) Is it possible to concentrate and recover nutrients with two stage nanofiltration process and continuous electrodialysis process without any precipitation chemical additions or significant membrane fouling.

1.3 **Outline**

This thesis focuses on finding advanced technologies for enhanced micropollutant removal and nutrient recovery in municipal wastewater treatment. The publication I gives a broad review of potential technologies for the treatment of municipal wastewater effluents, especially membrane concentrates, main scope being in the recovery of value components from wastewater. However, the scope of the experimental part of this work will be in the potential membrane technologies and advanced oxidation processes for municipal wastewater treatment, which can provide solutions to the enhanced micropollutant removal and nutrient recovery without addition of extra chemicals. Therefore, only the following processes, being nanofiltration, reverse osmosis,

electrodialysis as membrane processes and pulsed corona discharge as advanced oxidation process, all also included in the publication I, are evaluated experimentally in this work. The exact evaluation of the energy consumption of membrane processes studied as well as the comprehensive cost analysis of different treatment technologies have been left out from the thesis either due to limitations in the equipment or due to insufficient cost data available on the technologies. Also, the analysis and determination of oxidation by-products in the pulsed corona discharge oxidation has been left out from the thesis as this topic is a complex matter and would have made the overall scope of the thesis too wide.

Currently there are also a few other important mega trends in municipal wastewater treatment than micropollutants and nutrient recovery, such as the fate of microplastics and antibiotic resistant bacteria in wastewaters. Although these topics are also briefly addressed in the publication I and are important topics to examine and consider in the future, they were not fully included to the scope and researched experimentally in this study to limit the scope of the experimental part of this thesis and to keep the structure of the thesis in balance. However, the removal of antibiotics trimethoprim and tetracycline from municipal wastewater effluents were analyzed and discussed in this study as they were present in significant and readily detectable concentrations in the target wastewaters, and thus could potentially cause some antibiotic resistance in the future.

2 Advanced municipal wastewater treatment

Conventional activated sludge processes (CAS) and membrane bioreactor processes (MBR) are traditional processes for municipal wastewater treatment which usually removes bulk organic constituents measured as chemical oxygen demand (COD) and total organic carbon (TOC) efficiently. However, as these traditional processes nowadays sometimes struggles to meet the tightening discharge limits for nutrients and various micropollutants are not removed efficiently some more advanced treatment is required. These treatment technologies include processes such as pressure driven membrane filtration, electrodialysis, forward osmosis, membrane contactors, advanced oxidation, adsorption, coagulation and crystallization, which have been studied for enhanced wastewater treatment for instance by improving the removal of nutrients or micropollutants from municipal wastewaters (publication I). The utilization of these and many other techniques for municipal wastewater treatment and especially on membrane concentrate treatment have been further discussed in the publication I. The focus of this study has been to examine technologies for micropollutant removal and nutrient recovery in municipal wastewater treatment, which could be utilized without addition of extra chemicals such as precipitation chemicals, coagulants and flocculants. Therefore, nanofiltration, reverse osmosis, shear enhanced membrane filtration and electrodialysis processes as well as pulsed corona discharge oxidation process have been further discussed in this chapter as possible technologies for micropollutant removal and/or nutrient recovery.

2.1 Nanofiltration and reverse osmosis

Nanofiltration and reverse osmosis are pressure-driven membrane processes, where semi-permeable membranes are used to retain dissolved constituents present in the feed water. They are frequently utilized for wastewater reclamation and reuse applications. In municipal wastewater treatment these processes are usually applied as a tertiary treatment stage as an effluent polishing step for instance to ensure that the discharge limits are met.

This tertiary membrane filtration is usually done with spiral wound modules, where commonly water recoveries around 50-80% are achieved (Dialynas et al., 2008; Umar et al., 2015), which corresponds to volume reduction factors (VRF) 2 to 5. Often the aim is to enhance the removal of constituents such as dissolved solids, organic carbon, inorganic ions and organic pollutants. The retention of these constituents is based on size exclusion, charge repulsion as well as physico-chemical interactions between solute, solvent and the membrane. (Barceló and Petrovic, 2008; Bellona et al., 2004; Dialynas et al., 2008; Malaeb and Ayoub, 2011; Umar et al., 2015)

Reverse osmosis (RO) membranes are the tightest membranes in liquid/liquid separation, which retain essentially all dissolved and suspended material. Thin-film composite RO membranes have usually above 99% NaCl retention and molecular weight cut-off (MWCO) is less than 50 Da (Baker, 2004; Wagner, 2001). Therefore, the separation with reverse osmosis, especially when considering the removal of organic pollutants, is mainly dominated by size exclusion. Nanofiltration (NF) membranes have usually 0-50% retention for NaCl and MWCO range for NF membranes are usually between 150-1000 Da. NF membranes are designed to retain multivalent ions such as SO_4^{2-} and PO_4^{3-} efficiently whilst the monovalent ions are often readily passing the membrane. Thus, due to characteristics of NF membranes the charge exclusion as well as physico-chemical interactions have often a significant role in the removal of organic and inorganic impurities from wastewater in addition to size exclusion. (Baker, 2004; Barceló and Petrovic, 2008; Bellona et al., 2004; Malaeb and Ayoub, 2011)

Various nanofiltration and reverse osmosis processes have been efficiently utilized as tertiary treatment technologies to enable municipal wastewater reclamation and reuse (Bellona et al., 2012; Bunani et al., 2013; Chon et al., 2012; Kappel et al., 2014; Xu et al., 2010), but also as a part of nutrient recovery process to recover phosphorus as magnesium ammonium phosphate (struvite) (Quist-Jensen et al., 2016). The removal of organic carbon, inorganic ions and nutrients have been improved significantly with these processes. Bunani et al., (2013) applied nanofiltration with CK (GE Osmonics, MWCO

150 Da), NF90 (DOW, MWCO 200 Da) and NF270 (DOW, MWCO 200-300 Da) membranes for a tertiary treatment of municipal wastewater treatment effluent (Table 1) from conventional activated sludge process (CAS). Cross-flow flat sheet SEPA CF-II membrane test unit was used in the study at 10 bar filtration pressure, which led to permeate fluxes up to 26.6, 49.3 and 81 L/m^2h for CK, NF90 and NF270 membranes. 96 L/h concentrate flow rate was used in the nanofiltration, corresponding to a cross-flow around 0.15 m/s based on the concentrate flow and filtration cell dimensions as stated by filtration cell manufacturer. The aim was to enable wastewater reuse as an irrigation water. Irrigation water standards (Table 1) could be met by all NF permeates, only exception being the permeate conductivity of 3380 µS/cm for the NF270 membrane (Bunani et al., 2013). Therefore, according to their study the nanofiltration is a potential technology for reuse of municipal wastewater effluents for irrigation purposes. Combination of membrane bioreactor (MBR) process and nanofiltration can also be a potential approach for wastewater reclamation in municipal wastewater treatment (Chon et al., 2012). Chon et al., (2012) showed in their study, that with MBR + NF treatment it was possible to efficiently remove nutrients (NF permeate N_{tot} 8.7 mg/L and P_{tot} 0.46 mg/L) and organics (permeate COD below detection limits, dissolved organic carbon DOC 0.4 mg/L) from municipal wastewater (COD 9.1 mg/L, DOC 14.6 mg/L, N_{tot} 27.2 mg/L and P_{tot} 2.2 mg/L) and enable wastewater reclamation.

Table 1   Wastewater reuse with nanofiltration. Properties of CAS feed effluent, average properties of NF permeates and irrigation water standards. (Bunani et al., 2013)

Parameter	Feed (CAS effluent)	CK permeate	NF90 permeate	NF270 permeate	Irrigation water standard
pH, -	8.1-8.4	7.6	7.6	8.2	-
Conductivity, µS/cm	6108-7816	2300	690	3380	< 3000
Chemical oxygen demand (COD), mg/L	20-31	7.2	4.5	5.9	-
Total organic carbon (TOC), mg/L	12-17	3.3	1.7	1.4	-
Na^+, mg/L	1004-1091	353	134	584	<920
Cl^-, mg/L	1789-1848	572	206	1038	<1065
PO_4^{3-}, mg/L	2.05-2.28	<0.05	<0.05	<0.05	<2

Similar observations for application of CAS + NF or MBR + NF processes for water reuse have been done in several studies (Alturki et al., 2010; Azaïs et al., 2014; Bellona et al., 2012; Chon et al., 2012, 2011; Gündoğdu et al., 2019; Kappel et al., 2014; Xu et al., 2010). From these studies it can be concluded that nanofiltration can in most cases provide good quality reuse effluent for irrigation purposes, especially when tight nanofiltration membranes such as NF90 (DOW) are used. This is because the high permeability NF such as NF270 membranes may not remove enough conductivity and monovalent ions such as nitrate from CAS or MBR effluent to enable reuse. If indirect potable reuse or reuse as industrial purposes is the aim then usually tight NF or RO is required according to Azaïs et al., (2014), Bellona et al., (2012) and Gündoğdu et al., (2019) in order to provide satisfactory effluent quality, such as conductivity < 700 µS/cm, total dissolved solids < 500 mg/L, TOC < 0.5 mg/L and N_{tot} < 5 mg/L, for reuse. However, the feasibility of NF or RO for water reuse needs to be considered separately in each case as the requirements for effluent purity varies significantly depending on the location and its legislation as well as from the purpose of water reuse.

As a very efficient membrane process the reverse osmosis can provide even higher quality effluent than nanofiltration, but in the cases where nanofiltration can provide satisfactory effluent quality for reuse purposes it is the preferred technology (Bellona et al., 2012). This is due to better energy efficiency of NF over RO. For instance, in the study of Bellona et al., (2012) it was demonstrated that in membrane based water reclamation it is possible to cut down the electricity costs from 0.25 $/m^3 to 0.13 $/m^3 and total treatment costs by 55 123 $/year when tertiary treatment with reverse osmosis (ESPA2) would be switched to low-pressure nanofiltration (NF270) in a 425 m^3/h water reclamation process, where disinfected and microfiltered tertiary effluent was treated with NF or RO. The total treatment cost of 0.1 $/m^3 with NF was smaller than for the RO at 0.12 $/m^3, even when factoring in membrane replacement costs for NF process but not for the RO process. However, the effluent quality with RO was significantly better. For instance, an average value of 0.33 mg/L for TOC and <0.25 cm^{-1} for UV_{254nm} were obtained for ESPA2 membrane permeate, whereas similar values for NF270 permeate were 0.62 mg/L for

TOC and <0.50 cm^{-1} for UV$_{254nm}$. The TOC value obtained for NF270 membrane exceeded the 0.5 mg/L limit stated in California Department of Public Health Draft Groundwater Recharge Requirements, considering 100% reclaimed water contribution and no dilution. In many cases there is some dilution factor applied in water reuse applications. The NF270 membrane also proved to have significantly smaller fouling tendency than ESPA2 membrane in addition to significant annual cost savings. Therefore, water reclamation with NF270 membrane may be a feasible and cost-efficient approach according to (Bellona et al., 2012)

When aiming for wastewater reclamation and reuse it is also important to make sure that all potentially harmful organic micropollutants such as pharmaceuticals, pesticides and hormones are removed from the effluent before reuse. Combination of CAS and traditional aerobic or anaerobic MBR processes as well as sequential batch reactors with nanofiltration and reverse osmosis processes have been studied in recent years for this task (Alturki et al., 2010; Azaïs et al., 2014; Chon et al., 2012, 2011; Comerton et al., 2008; Dolar et al., 2012; Kimura et al., 2004; Sahar et al., 2011; Sui et al., 2010; Wei et al., 2016, 2018; Yoon et al., 2007). Reverse osmosis with membranes such as TR70-4021-HF (Ropur membranes), BW30-400, TW30 25-40 (DOW Filmtec) and ESPA2 (Nittto Denko) can provide above 95% retention for micropollutants such as carbamazepine, diclofenac, atenolol, estradiols and DEET (N,N-diethyl-meta-toluamide), when effluents from MBR or CAS processes are treated (Alturki et al., 2010; Dolar et al., 2012; Sahar et al., 2011). As the separation of micropollutants in reverse osmosis is mainly due to size exclusion the high efficiency of reverse osmosis for micropollutants with molecular weights often above 150 g/mol can be expected. The efficiency of nanofiltration for micropollutant removal depends largely on the target molecule, water matrix and membrane properties, as removal rates from 30 to above 95% for different pollutants such as carbamazepine, diclofenac, atenolol, DEET and paracetamol/acetaminophen with NF90 and NF270 membranes (DOW Filmtec) have been reported in the literature (Alturki et al., 2010; Azaïs et al., 2014; Wei et al., 2018, 2016).

Thus, NF can also potentially provide efficient barrier to various micropollutants, but as the separation largely depends on the water matrix and the type and composition of pollutants present as well as membrane characteristics some more case by case research is required to determine the efficiency of NF for micropollutant removal. Most of the studies related to NF and RO have been focused on the application of these membrane processes as a traditional tertiary treatment after a CAS or MBR process applying precipitation chemicals for phosphorus removal. This makes resource recovery in municipal wastewater treatment more challenging. Another challenge with tertiary NF or RO treatment with spiral wound modules is that the achievable water recoveries are usually only between 50 to 80%, which leads to high volumes of membrane concentrate with a quite dilute nature in respect to valuable components such as nutrients. Thus, the membrane concentrates produced by NF and RO are often considered as waste streams rather than raw materials for a resource recovery.

2.2   Shear enhanced membrane filtration

In shear enhanced membrane filtration moving parts such as rotating discs, rotors, rotating membranes or vibration is utilized to create high turbulence on the membrane surface. For example in rotating disc systems and vibratory shear enhanced processing technology (VSEP) shear rates around $1\text{-}3*10^5$ s^{-1} can be achieved (Ding et al., 2015; Jaffrin, 2008). Several different types of shear enhanced membrane modules have been developed, which have wider flow channels than in the spiral-wound modules traditionally used in tertiary membrane filtration processes. This enables the treatment of challenging and more concentrated effluents and makes higher water recovery rates possible. This feature could be also utilized in municipal wastewater treatment to achieve higher water recoveries compared to 50-80% achieved by spiral wound modules as well as to concentrate nutrients present in the concentrates to enable resource recovery. By creating high turbulence on the membrane surface the formation of concentration polarization layer is decreased in shear enhanced membrane filtration, the permeate flux is increased, and additionally the membrane fouling can be potentially decreased as well as the formation of unwanted precipitates on the membrane can be prevented. (Ding et al., 2015;

Jaffrin, 2012, 2008; New Logic Research Inc, 2013) Further discussion about shear enhanced membrane filtration and its features is also found in the publication I.

Different shear enhanced membrane processes such as vibratory shear enhanced processing technology (VSEP), cross-rotational (CR) filters and multishift disk systems (MSD) have been utilized for the treatment of various demanding effluents and waste streams for instance to prevent fouling or to maximize water recovery. These effluents include municipal wastewater effluents (Mänttäri and Nyström, 2007), landfill leachates (Chan et al., 2007; Zouboulis and Petala, 2008), brackish water RO concentrates (Subramani et al., 2012), dairy wastewaters and process waters (Akoum et al., 2004; Luo and Ding, 2011), detergent wastewaters (Luo et al., 2012), mineral suspensions (Ding et al., 2006) as well as various pulp and paper industry effluents like black liquor and acidic clear filtrate (Bhattacharjee and Bhattacharya, 2006; Huuhilo et al., 2001; Kallioinen et al., 2010; Mänttäri et al., 2008).

Although there are numerous application areas of shear enhanced membrane filtration and various different module types only limited amount of research exists in the field of municipal wastewater treatment. Mänttäri and Nyström (2007) utilized CR filter (laboratory scale CR250 with 0.09 m^2 membrane area) equipped with nanofiltration (NF270, DOW) and reverse osmosis membrane (ESPA 3, Hydranautics) for the tertiary treatment of municipal wastewater effluent and maximization of water recovery. High VRF values of 15-18 (corresponding to water recovery rates of 93.3-94.4%) were achieved in the filtration experiments with the CR250 filter. Both NF and RO membranes were able to remove organics measured as COD and TOC efficiently, retentions being between 94 and 100% for NF270 and ESPA 3 membranes. ESPA 3 membrane performed better for the removal of inorganic matter, retention being 98% for inorganic matter in total compared to the 88% measured for NF270 membrane. However, significantly lower fouling tendency was observed for the NF270 membrane, being only 6% in the treatment of municipal wastewater effluent whereas the similar value for ESPA 3 membrane was 45%. (Mänttäri and Nyström, 2007)

Only limited amount of literature exists related to shear enhanced membrane filtration, such as CR nanofiltration, of municipal wastewater effluents. Yet shear enhanced membrane filtration shows great potential to achieve very high water recoveries in tertiary municipal wastewater treatment. Potentially it also enables concentration of nutrients whilst preventing the formation of unwanted precipitates on the membrane during concentration of municipal wastewater effluents. Therefore, CR nanofiltration could be an efficient process for the minimization of membrane concentrate volume and concentration of nutrients, namely phosphorus. In cross-rotational filter rotor blades are used to create the turbulence on the membrane surface (Fig. 3). Rotors inside the module are often rotating at the speed of 500-1000 rpm (peripheral velocity up to 10-15 m/s), which creates very turbulent conditions inside the module and enhances the permeate flux as well as potentially decreases fouling tendency and enables higher water recoveries.

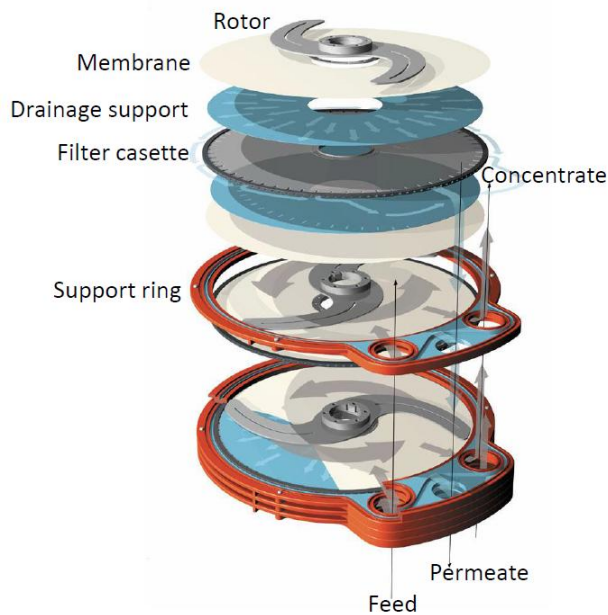Fig. 3   Schematic structure of CR filter. (Nurminen, 2011)

Although high shear rates and water recovery rates can be obtained by shear enhanced membrane filtration, it comes with a cost, as extra amount of energy is required for vibrating the membrane module or rotating the rotors when compared to traditional spiral wound modules. For instance, the full scale VSEP RO module of 150 m^2 applied for

wastewater treatment utilize 16 kW feed pump and total energy consumption is around 2.5 kWh/m^3 (Jaffrin, 2008). VSEP technology maximizes the vibrations by using resonant frequency and the power consumed by vibrating a module can be only 9 kW for a modules up to 150 m^2 of membranes (Ding et al., 2015). In addition to energy requirements the shear enhanced membrane processes in some cases also suffer from high costs and process complexity, especially when disks rotate between fixed membrane. In some cases also the availability of industrial scale modules is limited as only few modules such as CR, VSEP and MSD modules are available with a membrane area above 100 m^2 per module. (Ding et al., 2015; Jaffrin, 2012, 2008)

2.3 **Electrodialysis**

Electrodialysis (ED) is an emerging electrochemical membrane technology, where an alternating series of cation exchange membranes (CEMs) and anion exchange membranes (AEMs), which are placed between terminal cathode and anode, are used to separate and concentrate ions for instance to desalinate water or to concentrate nutrients (Fig. 4). Current is applied between the electrodes via potentiostat, which generates an internal potential gradient causing ions to migrate through electrodialysis membranes. Major application areas of ED have been traditionally in the field of brackish water desalination, table salt production, industrial process water demineralization and wastewater treatment, whereas emergent ED applications aim to concentrate nutrients from various waste streams. (Baker, 2004; Batstone et al., 2015; Mehta et al., 2015; Strathmann, 2010, 2004; Xie et al., 2016)
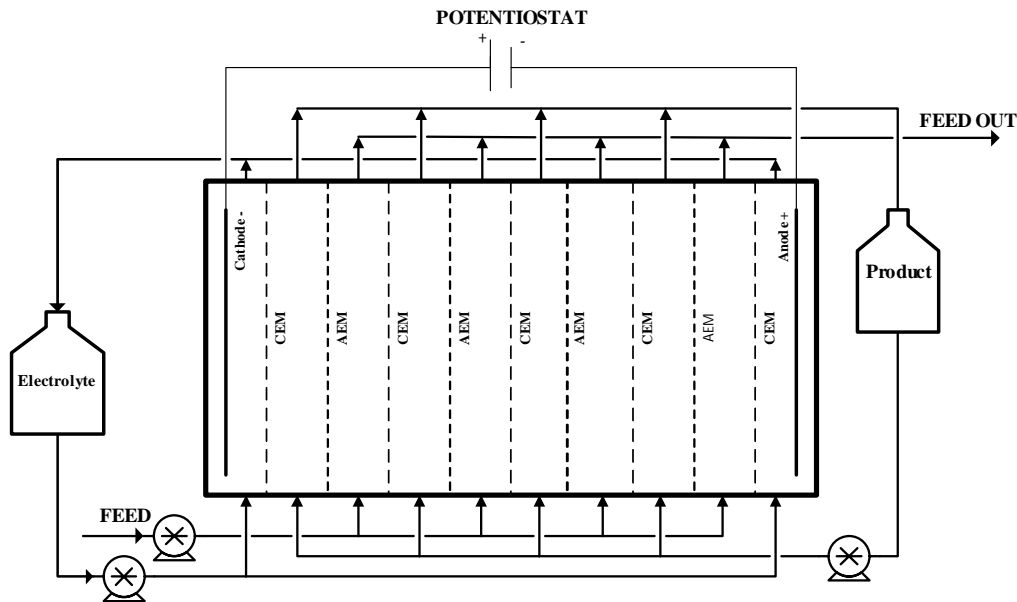
Fig. 4   Schematic diagram of electrodialysis.

Electrodialysis has been utilized for the concentration and recovery of nutrients such as ammonia and phosphorus for potential fertilizer purposes from various streams such as municipal wastewater effluents, swine manure, urine as well as various synthetic feed streams like simulated RO concentrates (Ebbers et al., 2015; Ippersiel et al., 2012; Linden et al., 2019; Mondor et al., 2008; Pronk et al., 2007; Thompson Brewster et al., 2017; Wang et al., 2015; Zhang et al., 2013, 2009). Several researchers have utilized both lab and pilot scale electrodialysis to concentrate nutrients, mainly ammonia, present in manure/urine and achieved concentration factors 2.8, 3.2, 3.5, 4.1 and 6.7 for ammonia (Ippersiel et al., 2012; Mondor et al., 2008; Pronk et al., 2007, 2006). Highest concentration of ammonia nitrogen, being 21.35 g/L, with ED has been reported by Ippersiel et al., (2012), who concentrated ammonia 6.7 times (3.2 g/L in the swine manure feed) with laboratory scale batch electrodialysis utilizing AR204SZRA anion exchange and CR67HMR cation exchange membranes from Ionics (10 cell pairs, 220 cm^2 per membrane, voltage 17.5 V, current density 40 mA/cm^2). On average 95% of the total ammonia nitrogen present in the swine manure could be recovered by ED. Further

concentration of ammonia with ED was limited by water transfer (0.81 L per batch, 9.6% of the initial manure volume) by osmosis and electro-osmosis (Ippersiel et al., 2012).

Although promising concentration factor for ammonia was reached by Ippersiel et al., (2012) the results from the other studies have been more modest. Mondor et al., (2008) achieved only 2.8 times concentration for ammonia (from 5.14 g/L to 14.25 g/L) with ED and concluded that the ammonia concentration was partly limited by osmosis as well as the transfer of solvated ions from manure to the concentrate solution. This caused water transport from the dilute (manure) to the concentrate compartment. Major reason limiting the maximum ammonia concentration was however volatilization (17% of the ammonia volatilized) (Mondor et al., 2008). Another challenge when applying ED for the concentration of ammonia from manure have been membrane fouling such as membrane surface fouling. However, the fouling has been significant issue mainly only during long term ED operation of several months. (Ippersiel et al., 2012; Mondor et al., 2008; Pronk et al., 2007)

Electrodialysis has been also studied as a technology to concentrate and recover nutrients such as phosphorus from municipal wastewater effluents (Ebbers et al., 2015; Thompson Brewster et al., 2017; Zhang et al., 2013). Similar concentration factors for phosphorus as for ammonia in the ED treatment of manure has been achieved in the ED studies with municipal wastewaters. For instance Zhang et al., (2013) reported 2.7 times concentration of phosphorus (from 0.24 g/L to 0.65 g/L) when upflow anaerobic sludge blanket reactor effluent was treated with ED. According to Linden et al., (2019) the limiting effect of osmosis and back diffusion to the concentration of nutrients can be reduced by operating ED at dynamic current density instead of a fixed current density. The concentration factor for ammonia could be increased from 4.5 to 6.7, when dynamic current density was used in ED of synthetic anaerobic sludge reject water (Linden et al., 2019). ED membrane fouling and scaling can be a significant challenge when electrodialysis is used for nutrient concentration and recovery in municipal wastewater treatment similarly as in the ED treatment of manure or urine. However, it can be controlled and minimized for instance

by combining pre-treatment such as struvite crystallization with ED to lower the risks for precipitation of phosphates as well as by pH adjustment such as pH lowering below 7 to lower risks for scaling due to precipitation. (Thompson Brewster et al., 2017)

Before utilizing the nutrient rich products produced by ED for fertilizer purposes it is also important to study if harmful pollutants such as pharmaceuticals can be present in the ED product. Only few studies have been conducted which examine the fate of micropollutants during ED treatment of wastewaters (Banasiak et al., 2011; Banasiak and Schäfer, 2010; Pronk et al., 2007, 2006). According to Pronk et al., (2006), who studied the removal of micropollutants propranol, ethinylestradiol, diclofenac, ibuprofen and carbamazepine during the ED treatment of anthropogenic urine (target pollutants spiked to feed at concentration up to 10 µM equaling to >2 mg/L), various micropollutants such as ethinylestradiol, diclofenac and carbamazepine can be efficiently excluded (>90% removal) from the nutrient rich concentrate product, when nutrients in urine are concentrated with ED. Although the pollutants were removed efficiently, a significant breakthrough of pollutants propranolol and ibuprofen occurred after longer operating times of 90 days (>40% of the pollutant amount in the concentrate product). Ethinylestradiol, which was removed efficiently, was the only micropollutant out of the studied pollutants which is included to the European commission's 2nd watch list of priority pollutants to be monitored from the surface waters of EU (European Commission, 2018). For analytical purposes the spiked concentrations of pollutants were significantly higher than the real environmental concentration. Therefore, the permeation of pollutants can be expected to be lower when concentrations are lower and close to environmental concentrations. This is because the adsorption/partitioning (effected by molecule hydrophobicity/hydrophilicity) was identified as major pollutant removal mechanism together with sieving and electrostatic interactions. (Pronk et al., 2006)

Unfortunately, only limited amount of research has been conducted with the electrodialysis of real municipal wastewaters for nutrient concentration and recovery, especially on a pilot or full scale. Also, the possible transport of micropollutants, present

at ambient concentrations in the feed, during electrodialysis treatment of real wastewaters must be studied in future research before it can be concluded if ED is suitable treatment technology for municipal wastewater treatment.

2.4 Pulsed Corona Discharge

Advanced oxidation processes (AOPs), such as non-thermal plasma oxidation process pulsed corona discharge (PCD), are techniques where highly reactive radicals, mainly hydroxyl radicals and ozone, are utilized at ambient temperature and pressure to oxidize and degrade organic impurities, such as micropollutants, present in water or wastewater. Depending on the way of generating the radicals the AOPs can be classified as ozone based, hydrogen peroxide based, photocatalysis, ultrasound, electron beam, electrochemical and non-thermal plasma oxidation processes. Out of the two main radicals the hydroxyl radical ($\cdot$OH) is very effective and non-selective chemical oxidant, which reacts readily with most organic substances. It has a very high oxidation potential of 2.80V (ozone 2.07V). (Black & Veatch Corporation, 2010; Crittenden et al., 2012; Ribeiro et al., 2015)

Many traditional advanced oxidation processes can be either energy intensive as discussed in the publication I or then challenging to operate for instance due to continuous addition of chemicals. Therefore, new less complex oxidation processes minimizing the amount of chemicals used in oxidation, such as pulsed corona discharge oxidation (PCD) have been developed. Pulsed corona discharge (Fig. 5) is a non-thermal plasma oxidation process, where strong oxidants $\cdot$OH radicals and ozone are generated *in situ* in a simple manner without separate addition of chemicals. High voltage electrodes are used in the PCD process to ionize the liquid surrounding the electrodes and conductive region is formed, where the discharge is released. High voltage pulse generators are used to create short-term electric pulses (100 ns), which triggers the oxidation reactions inside the PCD reactor. These oxidation reactions can be enhanced by dispersing the feed water solution as water droplets through jets and the process efficiency can be further increased by using

oxygen rich atmosphere in oxidation instead of air. (Panorel et al., 2013a, 2013b, 2011; Preis et al., 2013)
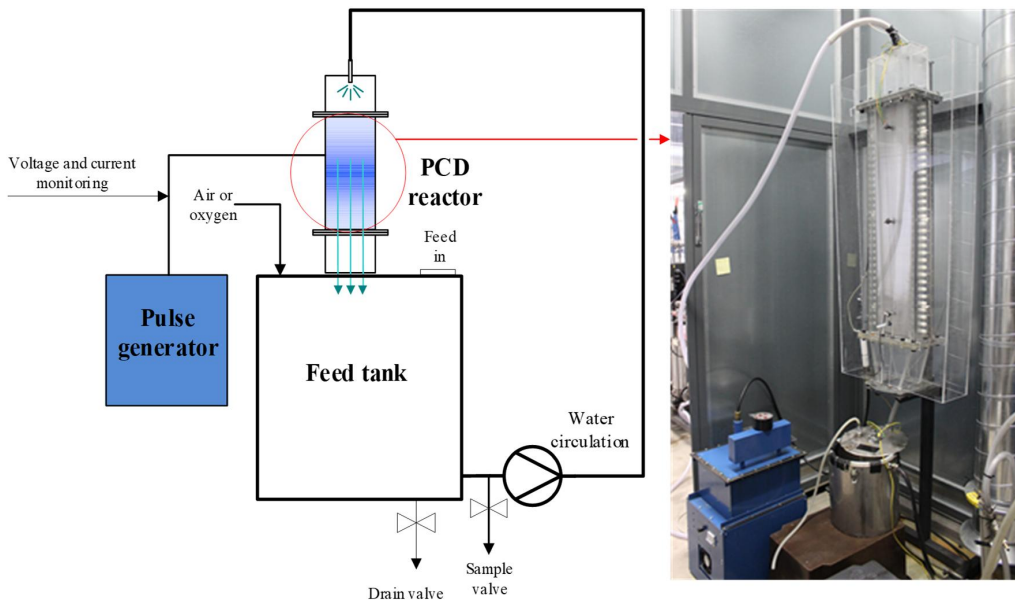
Fig. 5   Process schematic of pulsed corona discharge.

PCD oxidation has been studied for various applications such as for the degradation of humic substances, lignin, phenol and various micropollutants such as pharmaceuticals ibuprofen, diclofenac and carbamazepine as well as hormones such as 17-alpha-ethinylestradiol (EE2) and 17-beta-estradiol (E2) from different aquatic solutions (Ajo et al., 2018, 2016; Banaschik et al., 2015; Dobrin et al., 2013; Panorel et al., 2014, 2013b, 2013a, 2011; Preis et al., 2013; Singh et al., 2017; Zeng et al., 2015). Out of these pharmaceuticals and hormones mentioned the 17-alpha-ethinylestradiol and 17-beta-estradiol are both in the European commission's 2nd watch list of priority pollutants (European Commission, 2018), whereas the pharmaceuticals ibuprofen, diclofenac and carbamazepine has been widely studied as they are either very frequently used (ibuprofen and diclofenac) or then very poorly biodegradable and thus accumulating in the aquatic environment (carbamazepine and diclofenac). PCD has proven to be very efficient oxidation method to degrade humic substances and lignin as Panorel et al., (2011) achieved over 95% degradation for humic acid with PCD oxidation (efficiency 20-60

g/kWh) of aqueous humic acid solution (humic acid 3-23 mg/L) and similarly Panorel et al., (2014) reported very high efficiencies of 17-44 g/kWh (air atmosphere) and 55 g/kWh (89% oxygen atmosphere) for the oxidation of aqueous lignin with PCD. These efficiencies are significantly higher than reported for traditional ozonation, being <10 g/kWh for ozonation of humic substances and 7-25 g/kWh for ozonation of lignin (Panorel et al., 2014, 2011). Therefore, PCD oxidation could be a more energy efficient alternative to ozonation for the applications were organic pollutants needs to be degraded.

PCD oxidation has also performed well, mainly due to strong oxidation power of hydroxyl radicals, when aqueous solutions containing micropollutants such as carbamazepine, diclofenac, ibuprofen and paracetamol has been treated (Ajo et al., 2016; Dobrin et al., 2013; Panorel et al., 2013a, 2013b). Even complete degradation of pollutants such as carbamazepine (5 µg/L) and paracetamol (100 mg/L) can be achieved with PCD when aqueous pollutant solutions are treated by using only moderate amount of energy (1-2 kWh/m^3) (Ajo et al., 2016; Panorel et al., 2013b). However, most of the research conducted up to date related to PCD has been done with model/synthetic aqueous solutions, where the effect of effluent organic matter is usually limited and the concentration of target pollutant is often an order of magnitude higher than in the real wastewaters, or with real wastewaters spiked with target pollutants (Ajo et al., 2016; Banaschik et al., 2015; Dobrin et al., 2013; Panorel et al., 2014, 2013a, 2013b, 2011; Preis et al., 2013; Singh et al., 2017; Zeng et al., 2015).

Pulsed corona discharge shows great promise as an efficient advanced oxidation method, but in order to evaluate its efficiency properly more research with real wastewaters is required to confirm both the degradation efficiency as well as the energy efficiency in real matrix with effluent organic matter. Ajo et al., (2018) utilized PCD oxidation for the degradation of 32 different pharmaceuticals and hormones such as pharmaceuticals atenolol, carbamazepine, caffeine, diclofenac, ibuprofen and hydrochlorothiazide as well as hormones 17-alpha-ethinylestradiol and 17β-estradiol, from raw sewage of a public hospital as well as biologically treated effluent from a health-care institute. PCD

oxidation proved to be very efficient as ≥87% removal of target compounds (excluding caffeine) was achieved in the oxidation of raw sewage with 1 kWh/m^3 and 100% removal of all target pollutants, including hormones 17-alpha-ethinylestradiol and 17β-estradiol present in the European commission's 2nd watch list of priority pollutants, was achieved when the biologically treated effluent was treated with PCD by using only 0.5 kWh/m^3 of energy (Ajo et al., 2018).

According to literature the PCD oxidation seems to be very promising emerging advanced oxidation technology for micropollutant degradation from municipal wastewater effluents. However, currently there is not enough research data related to PCD treatment of real municipal wastewater effluents not spiked with target pollutants. Therefore, further research related to the degradation of micropollutants, present in the municipal wastewaters at natural concentrations, with pulsed corona discharge needs to be executed before the suitability of the PCD oxidation as a post treatment technology for municipal wastewater effluents can be confirmed.

3 Materials and methods

3.1 Feed effluents

Various feed effluents were utilized in this work varying from raw municipal sewage to synthetic wastewater. In publication II raw sewage after sand removal and pre-screening was used as feed for the conventional activated sludge (CAS) process as well as membrane bioreactor (MBR) processes described in the sections 3.2 and 3.3. MBR permeates produced by two different process lines of MBR pilot, process line A without and line B with chemical precipitation, were used as a feed for two-stage nanofiltration (NF) concentrating phosphorus (publication III) and to pulsed corona discharge (PCD, publication II) process described in the following sections. Final nutrient rich NF concentrate from publication III was used as a feed for PCD oxidation in publication IV. For pilot scale electrodialysis (ED, publication V) a centrate wastewater after struvite precipitation was used as a feed. Before struvite precipitation the wastewater originated from the centrifugation of anaerobically digested sludge. In publication VI a synthetic wastewater simulating the properties of centrate after struvite precipitation (publication V) was used as feed effluent for the laboratory scale ED to examine the transport of pharmaceuticals across ED membranes in a controlled water matrix. All processes mentioned above are discussed in more detail in the following sections 3.2 and 3.3. The properties of the feed effluents used in this work are presented in the Table 2.

Table 2   Average properties of the feed effluents used in the study. [a]Effluents studied contained several different micropollutants, micropollutants presented below are examples of common pollutants (average concentrations) found in municipal wastewaters. [b]Phosphorus measured as soluble PO_4^{3-}-P and [c]nitrogen measured as soluble NH_4^+-N.

Parameter	CAS influent (MBR feed in publication II)	MBR permeate A (NF feed in publication III)	MBR permeate B (PCD feed in publication II)	NF270 concentrate (PCD feed in publication IV)	Centrate after struvite precipitation (ED feed in publication V)	Synthetic wastewater (ED feed in publication VI)
pH [-]	7.4	7.0	6.8	5.9	8.5	8.5
Conductivity [µS/cm]	861	534	764	12 670	8 300	10 300
DOC [mg/L]	80.7	9.5	7.4	2 130	-	-
COD [mg/L]	460	22	18	5 930	351	-
Biological oxygen demand, BOD_7 [mg/L]	178	<2	<2	74	-	-
BOD_7/COD ratio [-]	0.39	<0.09	<0.11	0.01	-	-
P_{tot} [mg/L]	12	4.4	0.15	380	58[b]	4.8[b]
N_{tot} [mg/L]	73	23	37	190	835[c]	756[c]
Ca^{2+}, mg/L	-	-	-	663	25	4.6
Mg^{2+}, mg/L	-	-	-	629	1.0	-
K^+, mg/L	-	-	-	-	232	196
Na^+, mg/L	-	-	-	-	1003	933
Cl^-, mg/L	-	-	-	-	15	-
Micropollutants[a]						
Diclofenac [µg/L]	1.6	1.1	2.0	410	-	11.3/108
Carbamazepine [µg/L]	0.45	0.6	1.0	33	-	12.2/107
Furosemide [µg/L]	16	13.6	12.8	580	-	11.0/108
Metoprolol [µg/L]	1.9	1.2	1.5	78	-	10.4/99
DEET [µg/L]	0.32	0.009	0.02	1.1	-	-

3.2   Equipment and execution of the experiments

An MBR pilot unit (Alfa Laval) which contained two separate process lines, first line a MBR without chemical precipitation of phosphorus (process concept A) and second one a MBR with chemical precipitation of phosphorus (process concept B), was operated in parallel with a full-scale conventional activated sludge process (CAS) in a small municipality in Finland (publication II, Fig. 6). MFP2 polyvinylidene fluoride (PVDF)

microfiltration membranes from Alfa Laval (pore size 0.2 µm, average permeability > 500 L/(m^{2}h bar), and contact angle around 80°) were used in the MBR pilot. In the second MBR process line the removal of phosphorus was done by adding 300 mg/L of ferric sulfate to the denitrification stage (PIX-105, Kemira Oyj). The process parameters used in the biological wastewater treatment processes studied in this work are presented in the section 3.3. A 2.5" nanofiltration spiral wound module containing the NF270 membrane from DOW was used in the NF process to treat the MBR permeate from the first MBR process line (process concept A, Fig. 6). The NF270 membrane has a cross-linked semi-aromatic polyamide active layer on a polysulfone support. The molecular weight cut-off (MWCO) value of the NF270 membrane is 220–250 Da, the contact angle is 30° and the membrane is negatively charged at neutral pH area (isoelectric point 2.7). (Azaïs et al., 2014; Mänttäri et al., 2006, 2004). (publication II)
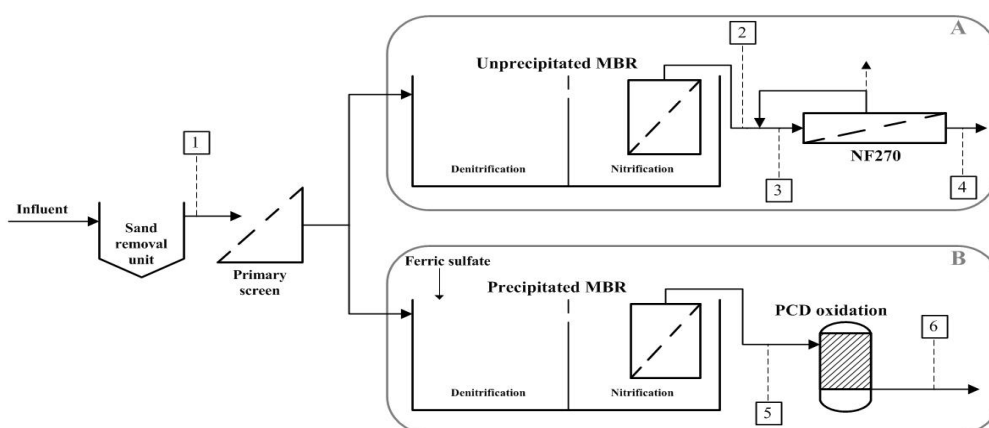
Fig. 6   Studied process concepts (A and B) for enhanced micropollutant removal from municipal wastewater (publication II). The sampling points for micropollutant research are marked with numbers 1–6. The 7th sampling point was treated effluent from the CAS process.

The MBR permeate (process concept B, publication II) was further treated by the non-thermal plasma advanced oxidation method in the form of gas-phase pulsed corona discharge (PCD, Figs 5 and 6). Oxidation was used to degrade the micropollutants present in the MBR permeate. Degradation of micropollutants during pulsed corona discharge occurs in a PCD reactor, where ozone and ·OH radicals are generated from oxygen and water by using small energy input from a pulse generator. The high voltage pulse generator creates short-term electric pulses (100 ns), which are discharged inside the PCD

reactor via electrode wire. The reactor has an inside volume of 0.034 m^3 and it utilizes conventional wire-plate corona geometry, where stainless steel electrode wires are horizontally positioned between vertical grounded plate electrodes. The electrode wires have a 0.5 mm diameter and are placed at 30 mm distance from each other and 17 mm from the grounded plate electrodes. The discharge propagates in the gap between the electrodes, where the highly reactive oxidants ozone and hydroxyl radicals are formed in the plasma. In the PCD process the aqueous solution to be treated (MBR permeate and NF concentrate in this study) is pumped to the top of the PCD reactor and dispersed to the reactor by a simple perforated plate. The solution will flow in jets and droplets inside the reactor between electrodes to the zone of the gas-phase pulsed corona discharge formation, where the organic target compounds reacts with the ozone and ·OH radicals.

Laboratory scale reverse osmosis experiment was also executed to support the promising results from publication II concerning micropollutant removal with the nanofiltration and pulsed corona discharge and to compare results of nanofiltration to reverse osmosis. This was done by treating MBR permeate (process concept B, publication II, batch sample) with reverse osmosis in a laboratory scale DSS Labstak M20 filter, which is a plate and frame filter designed for testing several membranes in parallel (especially NF and RO). Three reverse osmosis membranes being AK (GE), BW30 and SW30 (DOW Filmtec) were utilized in the filtration experiment which was conducted at following conditions: filtration temperature 25–30 °C, transmembrane pressure 12.3–12.7 bar, recovery rate ≤10% (initial feed volume 90L, total volume of final permeates 9L), cross-flow 1.4 m/s. The properties of the RO membranes used are presented in the Table 3. Filtration was done in a steady flux (target flux 30–45 L/m^{2}h) and permeates were collected from each RO membrane in parallel. 20 min stabilization time was used after pressure adjustment before the collection of the permeates was started. Filtration experiment was stopped after 3L of permeate had been collected from each membrane. Average fluxes for the RO membranes during the filtration were 28 L/m^{2}h for AK, 33 L/m^{2}h for BW30 and 44 L/m^{2}h for the SW30 membrane, respectively. Collected permeate samples were analyzed after the experiments for their pH, conductivity, COD, TOC, N_{tot}, P_{tot} and micropollutants.

Table 3 Properties of the reverse osmosis membranes used in laboratory scale filtration of MBR permeate to study micropollutant removal. Data from the manufacturers and (Akin and Temelli, 2011; Tu et al., 2011).

Parameter	Membrane		
	AK, GE Osmonics	BW30, DOW Filmtec	SW30, DOW Filmtec
pH range, -	4-11	2-11	2-11
Maximum temperature, °C	50	45	45
Maximum filtration pressure, bar	27.6	41	69
Nominal sodium chloride (NaCl) retention, %	>98	99.5	99.4
Contact angle, °	65	55	62

MBR permeate from municipal wastewater treatment process was used as feed effluent for the tertiary nanofiltration (Fig. 7, publication III). MBR permeate originated from a MBR process operated without chemical phosphorus removal (process concept A, Fig. 6). This enabled the phosphorus recovery from the final NF concentrate. Tertiary stage nanofiltration utilized NF270 membrane (DOW) in the 2.5" spiral wound module (up to VRF 6) with a membrane area of 2.6 m^2. The NF270 membrane was also used in the concentration filtration of nanofiltration concentrate (VRF 6) with a cross rotational CR350 filter (total membrane area of 1 m^2) to produce the final VRF 300 concentrate (Fig. 7). (publication III) The NF concentrate produced by the shear enhanced CR nanofiltration (publication III) was further treated with pulsed corona discharge oxidation (publication IV). PCD oxidation of NF concentrate was conducted with a similar PCD oxidation setup as used in the publication II (Fig. 5).
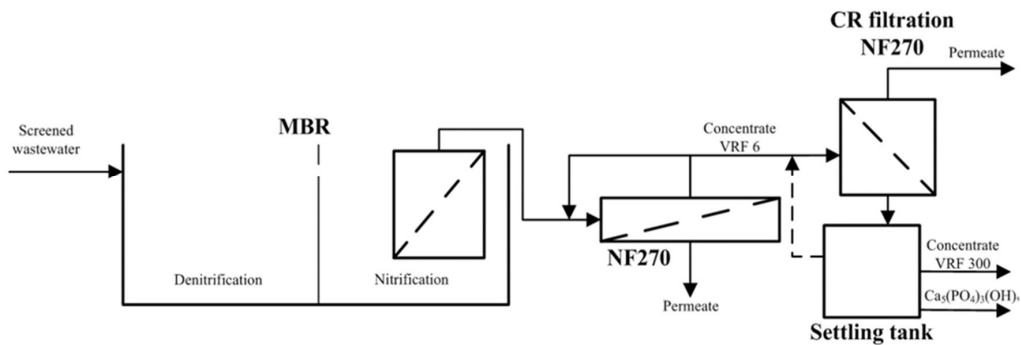

Fig. 7 Municipal wastewater treatment process utilizing shear enhanced nanofiltration (cross-rotational CR350 filter) for the minimization of membrane concentrate volume and recovery of nutrients (publication III).

A 30-cell pair pilot scale ED unit was utilized for the experimental work in the publication V (Fig. 8). The pilot ED unit was supplied by ABR Process Engineering (Brisbane, Australia) and equipped with 31 CEM membranes (General Electric CR67) and 30 AEM membranes (General Electric AR204SZRA) with an effective membrane area of 0.12 m^2 per membrane. CEM membranes were placed next to the cathode and anode in order to minimise the transfer of chlorine anions into the electrode chambers. Thick 6 mm spacers were used to minimise clogging and fouling that may occur when treating centrate wastewater (Thompson Brewster et al., 2016). Two mesh titanium/platinum iridium oxide (Ti/PtIrO$_2$) electrodes (295 x 400 x 1.5 mm) were used as the anode and cathode (ABR Process Engineering). 200 L high-density polyethylene tanks were used for the centrate feed tank, and recirculated electrolyte rinse solution as well as recirculated concentrate product. A 100 L high-density polyethylene tank was used to collect the feed out from the ED cell for sampling purposes before it overflowed to a sewer drain. All reservoir tanks were vented to maintain atmospheric pressure. A process logic controller (cRIO-9066 CompactRIO controller, National Instruments) and LabVIEW software (National Instruments 2015) was employed to control, operate and log operational data from the system. Each ED trial was executed as continuous 72 h process. The ED cell was cleaned by recirculating 0.5% sodium hypochlorite solution (NaOCl) for 2 h in the ED cell followed by recirculation of 1% hydrochloric acid (HCl) solution overnight after each 72 h cycle. (publication V)
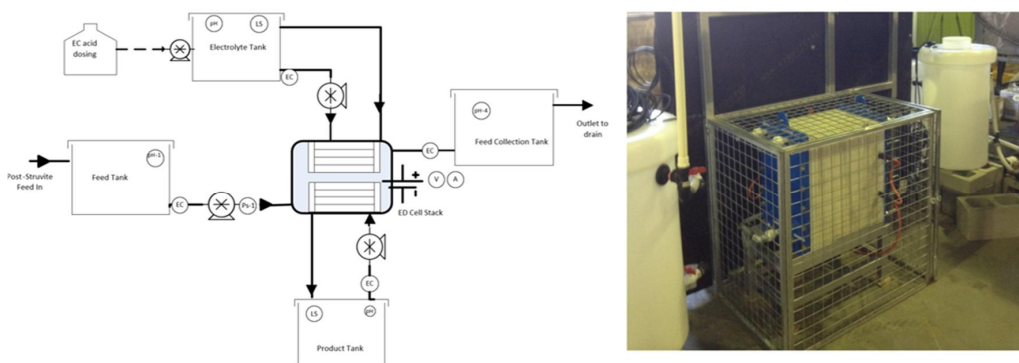

Fig. 8   Schematic drawing of pilot ED cell and associated dilute feed, concentrate product, electrolyte rinse solution and post ED cell dilute stream tanks. Electrical conductivity (EC), pH (pH), pressure transducer (PS), amperage (A) / voltage (V) transducers and ultrasonic level sensors (LS) are shown. (publication V)

Laboratory scale ED unit was utilized in a batch-mode ED experiments (publication VI). During these experiments the electrolyte, concentrate (hereafter named as product) and diluate were being recirculated through reservoirs. The unit was equipped with five CEMs (General Electric CR67) and four AEMs (General Electric AR204SZRA), each with an effective membrane area of 150 cm^2, and a 4 mm spacing. The anode and cathode were iridium mixed metal oxide (Ir MMO) mesh coated with titanium (ABR Process Development, Australia). The configuration of the ED unit consisted 4.5 cell pairs, an anode chamber, a cathode chamber, four product chambers and four feed chambers. Extra cation exchange membrane was fitted next to cathode chamber in order to prevent the migration of chloride ions into the electrolyte. The water reservoirs were ventilated to maintain atmospheric pressure. A potentiostat (Manson model HC3104) was used to supply a constant current to the ED system. Sulfuric acid (H_2SO_4, 1.5 mL/L) was used as electrolyte of which conductivity was maintained between 10 and 15 mS/cm during ED experiments by dosing 0.3–0.5 mL/L H_2SO_4 to the electrolyte reservoir when conductivity reached 10 mS/cm. (publication VI)

3.3   Process conditions

Process parameters for the biological processes studied in this work are presented in the Table 4. Table 5 provides process conditions for the nanofiltration and reverse osmosis processes studied in this work, whereas the process parameters for PCD oxidations carried out in this work are presented in the Table 6. Process conditions for the ED processes studied in this work are presented in the Table 7.

Table 4   Process parameters in the studied biological processes in the publication II. The presented values are average values during a micropollutant research period (n=3,) and the range is given in brackets, if applicable. The average dose of ferric sulfate was 300 mg/L in the MBR process B and process A was operated without phosphorus precipitation chemical dosing. The MBR processes were operated at a constant flux mode, and aeration was kept constant.

Parameter	CAS	MBR, concept A	MBR, concept B
Flux, L/(m^{2}h)	-	10	10
Mixed liquor suspended solids (MLSS), g/L	6	10 (8.6–11.1)	10 (7.6–11.1)
MBR aeration, Nm^3/h	-	6	6
pH in aeration	>6.5	6.8 (6.5–7)	6.8 (6.5–7)
Temperature in aeration, °C	8 (6–9)	10 (8–13)	10 (8-13)
Dissolved oxygen (DO), mg/L	>2	2.5 (2–3)	2.5 (2–3)
Sludge retention time (SRT), d	81 (79–83)	48 (33–57)	33 (24–39)
Hydraulic retention time (HRT), h	70 (67–74)	21	21

Table 5   Process conditions in the nanofiltration (NF270) and reverse osmosis (AK, BW30 and SW30) processes studied in this work (nanofiltration studied in publications II and III). Final recovery rate in the CR350 filtration 99.7% (concentration filtration from VRF6 to VRF300).

Parameter	NF270 membrane 2.5" Spiral wound module	NF270 membrane CR350 module	AK membrane DSS Labstak M20 filter	BW30 membrane DSS Labstak M20 filter	SW30 membrane DSS Labstak M20 filter
Average flux, L/(m^{2}h)	22 (13–31)	34 (15–55)	28 (26–30)	33 (30–35)	44 (42–48)
Transmembrane pressure (TMP), bar	5.4 (2–12)	4.3 (2.5–6.6)	12.5 (12.3–12.7)	12.5 (12.3–12.7)	12.5 (12.3–12.7)
Recovery rate, %	84 (68–92)	98	≤15	≤15	≤15
Average filtration temperature, °C	14 (9–17)	26 (18–32)	29 (27–30)	29 (27–30)	29 (27–30)
Feed water pH, -	7.0	7.1	6.5	6.5	6.5
Feed water conductivity, mS/cm	0.53	1.05	0.70	0.70	0.70

Table 6   Process parameters in the pulsed corona discharge oxidations carried out in this work. PCD oxidations conducted at room temperature (20 °C).

Parameter	Oxidation of MBR permeate, publication II	Oxidation of VRF300 NF concentrate, publication IV
Pulse repetition frequency, pps	840	840
Pulse duration, ns	100	100
Pulse amplitude, kV	20	20
Liquid flow rate, L/min	15	15
Average atmosphere composition, % O_2	91	89
Oxidation energy, kWh/m^3	0, 0.05, 0.1, 0.2, 0.5, 1.0	0, 0.3, 0.7, 1.5, 3.5, 10
Oxidation time, min	0, 1.5, 2, 3, 6, 11	0, 3.5, 8, 17, 38, 102
Feed water pH, -	6.3	5.9
Feed water conductivity, mS/cm	0.6	12.7
Feed volume, L	50	50

Oxygen atmosphere was used in the PCD oxidations instead of air atmosphere, since oxygen atmosphere enables enhanced generation of ozone and hydroxyl radicals and therefore increases degradation of organic molecules. Operating the PCD under air atmosphere over oxygen enriched atmosphere can also lead to higher nitrate (NO_3^-) concentration in the solution during oxidation due to mineralization of the nitrogen originating from the air. The increase in the energy consumption due to the production of oxygen atmosphere was expected to be minor compared to the use of air atmosphere. (Ajo et al., 2018; Dobrin et al., 2013; Panorel et al., 2013a, 2013b; Panorel, 2013)

Table 7   Process conditions in the electrodialysis experiments conducted in this work (publications V and VI).

Parameter	Pilot scale electrodialysis	Laboratory scale electrodialysis
Operating mode	Continuous	Batch
Total membrane area, m^2	7.3	0.14
Flow rate, L/h	75	1.4
Experiment duration, h	72	8
Constant current, A	2.5	0.5
Current density, A/m^2	20	33.3
Feed water pH, -	8.5	8.5
Feed water conductivity, mS/cm	8.2–8.4	10.1–10.5
Electrolyte H_2SO_4 target conductivity, mS/cm	10	10–15
Cell cleaning	0.5% NaOCl (2h) 1% HCl (overnight)	0.5% HCl (3h)

3.4 Analytical techniques

The analytical methods and equipment used in the analysis of effluent, wastewater and membrane concentrate samples taken during experiments of this study are presented in the Table 8.

Table 8   Analytical methods and equipment used in this work for the analysis of samples.

Analysis	Method	Equipment
pH, -	SFS 3021 - ISO 9001:2008	Metrohm 744 pH Meter (publications II, III, IV) BL391700 pH controller and HI2910B/5 pH probe Hanna Instruments (publication V) TDS Aqua-CPA pH meter (publication VI)

Electrical conductivity, mS/cm	SFS 3022 - ISO 9001:2008	Knick Konduktometer 703, 25 °C (publications II, III, IV) M200 transmitter and EASYSENSE cond77 probe, Mettler Toledo (publication V) TDS Aqua-CPA conductivity meter with k=10 sensor (publication VI)
Total organic carbon (TOC) and Dissolved organic carbon (DOC), mg/L	-	Shimadzu TOC-L total organic carbon analyzer, samples centrifuged (10 min, 3500 rpm) with an ELMI CM-6MT centrifuge (TOC) or prefiltered with 0.45 μm Nylon filters (DOC) before analysis (publications II, III, IV)
Specific UV absorbance (SUVA$_{254nm}$), -	-	JASCO V-670 UV-Vis-spectrophotometer at 254 nm, samples prefiltered with the 0.45 μm Nylon filter (publication II)
Chemical oxygen demand (COD), mg/L	COD LR/HR, DIN ISO 15705/SFS 5504 -	Hach DR2010 spectrophotometer at 420 (LR) or 620 (HR) nm (publications II, III, IV) Merck Spectroquant® COD cell tests (HC565173 25–1500 mg/L Spectroquant®) (publication V)
Biological oxygen demand (BOD$_7$), mg/L	SFS-EN 1899-1 (1998) and SFS-EN 25814 (1993)	Electrochemical probe method, analyzed in FINAS accredited environmental laboratory (T032, SFS-EN ISO/IEC 17025:2005), determination limit 2 mg/L (publications III and IV)
Total suspended solids (TSS), mg/L	APHA (1988)	Determined by standard methods (publication V)
Total nitrogen (N$_{tot}$), mg/L	(SFS-EN ISO 13395 (1997) FIASTAR AN 5202/2000) -	Flow injection analysis method (FIA), analyzed at FINAS accredited environmental laboratory (T032, SFS-EN ISO/IEC 17025:2005), determination limit 0.2 mg/L, error margin 10–20% (>0.36 mg/L) (publications II and IV) Analyzed with total nitrogen unit (TNM-L) of the Shimadzu TOC-L total organic carbon analyzer (publication III)
Ammonium nitrogen (NH$_4^+$-N), mg/L	-	Lachat QuickChem flow injection analysis (FIA) (Lachat Instruments, Loveland, CO, USA) for soluble NH$_4^+$-N (publications V and VI)

Total phosphorus (P_{tot}), mg/L	Inoperative standard SFS-3026 (1986)	Analysis based on digestion with peroxodisulphate, determined at FINAS accredited environmental laboratory (T032, SFS-EN ISO/IEC 17025:2005), determination limit 2 µg/L, error margin 10–20% (>7.5 µg/L) (publications II and IV)
	DIN EN ISO 6878	Spectroquant® Phosphate cell test, measurement with Spectroquant Nova 60 spectrophotometer (method 14729, total phosphorus) (publication III)
Phosphate phosphorus (PO_4^{3-}–P), mg/L	-	Lachat QuickChem flow injection analysis (FIA) (Lachat Instruments, Loveland, CO, USA) for soluble PO_4^{3-}–P (publications V and VI)
Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+), mg/L	SFS-EN ISO 14911	Ca^{2+} and Mg^{2+} analysis with Thermo Fisher ICS-1100 ion chromatography, IonPac CG12A (4 x 50mm) + CS12A (4 x 250mm) column and eluent 22mN H_2SO_4 (publication III)
	-	Ca^{2+}, Mg^{2+}, Na^+, K^+ analysis by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer Optima 7300DV, Waltham, MA, USA) after nitric acid digestion (publications V and VI)
Cl^-, mg/L	-	Ion chromatography (IC) with Dionex ICS-2100 IC system, Dionex, CA, USA (publication V)
Volatile fatty acids (VFA), mg/L	-	Gas chromatography (GC) with Agilent Technologies 7890A GC System, CA, USA (publication V)

Overall the uncertainty of the COD, phosphorus and nitrogen analyses were 10–30% depending on the sample matrix and sample concentration (Table 8). Total solution volumes in ED experiments for the concentrate product and electrolyte rinse solution were measured for experimental period in the publication V by ultrasonic level sensors (Echopod DL10 Ocean controls, Flowline Australia). Precipitate formed during the concentration filtration with CR350 filter (publication III) was analyzed by Hitachi SU3500 scanning electron microscope (SEM) and Thermo Scientific UltraDry SDD EDS energy dispersive X-ray spectroscopy (EDS). SEM images were taken by using 15 kV acceleration voltage and BSE detector. In the EDS measurement a dual detector, spot size of 1.5 X 1 mm and Pathfinder software was used. For the SEM and EDS analysis a small

amount of precipitate was pressed as a cake and measurements were taken from the surface of the cake. (publication III)

Additionally, a least squares linear regression analysis (Microsoft excel 2013, data analysis) was utilized in the publication IV to identify the determining parameters for the micropollutant degradation during PCD oxidation of NF270 concentrate. Linear regression, such as least squares regression, is a simple and widely used tool to explain the relationships between one dependent and few independent variables such as relation of micropollutant properties to pollutant biodegradation (Bertelkamp et al., 2016; Raposo, 2016; Yang et al., 2016). Spearman's rank correlation factor (r_s) was utilized to find the correlations between micropollutant properties and pollutant degradation rates (measured as slope, k, % of degradation to energy dose). Spearman's rank correlation factor (r_s) is a nonparametric statistical tool to measure a monotonic relationship between paired data. Spearman's rank correlation factor (r_s) have been used in wastewater treatment applications for instance to find correlations between wastewater parameters and oxidation by-products (Krebel et al., 2011).

The pharmaceuticals studied in this dissertation were determined by using solid phase extraction as a pretreatment, and ultra-performance liquid chromatography coupled with mass spectroscopy analysis (UPLC/MS/MS) for micropollutant identification (publications II, III and IV). The analysis method was based on the standards EPA 1694 and EPA 539 (modified). The pesticide N,N-diethyl-meta-toluamide (DEET) was determined by using solid phase extraction as pretreatment and by gas chromatography coupled with mass spectroscopy analysis (GC/MS/MS) for the micropollutant identification. The limit of detection (LD) for the pharmaceuticals and pesticide were between 0.001 and 0.5 µg/L, depending on the sample matrix and the micropollutant to be analyzed. The uncertainty of the analysis was 30% for pharmaceuticals and 24% for DEET. (publications II, III and IV)

Target micropollutants studied in publication VI were analyzed by ultra-fast liquid chromatography (UFLC) coupled with mass spectrometry (MS). The analysis was conducted with Shimadzu UFLC connected to an AB Sciex 4000QTrap QLIT-MS equipped with a Turbo Spray source. Each sample was analyzed separately in both positive and negative ion multiple reaction monitoring (MRM) mode. Two transitions were monitored in the MRM mode. The first transition was used for quantification and the second one for confirmation purposes only. The quantification was performed using 8 point external calibration curves obtained from the injection of standard solutions ranging from 0.1 to 100 μg/L. Linear or quadratic regression was used depending on the compound, which gave good fits with R2 values above 0.99.

3.5   **Target micropollutants**

Micropollutants studied in this dissertation work (Table 9) included 16 pharmaceuticals and one pesticide. The main selection criteria for target micropollutants studied in each publication were frequency and occurrence in the municipal wastewater treatment effluents as well as stability (tendency for biological degradation) in traditional wastewater treatment processes. The aim was to choose micropollutants with different molecular properties and which can be detected from the treated effluents of traditional wastewater treatment. Thus, the selection of pollutants to be studied focused on the pollutants which may be biodegradable but are present in high concentrations in wastewaters and thus detectable after treatment, as well as pollutants which are –not easily biodegradable and inefficiently removed in traditional wastewater treatment.

The molecular properties and classification of the target micropollutants are presented in Table 9. Table 9 presents also the acid dissociation constants pKa, describing the acidity of a specific molecule. If the pKa value of a pollutant is lower than the pH of the wastewater or sludge, the pollutant will be dissociated and charged (Sui et al., 2010; Thomas and Foster, 2005). Log K_{ow} describes the hydrophobicity/hydrophilicity of a substance. If the log K_{ow} value is higher than 3.2, the substance is considered as clearly hydrophobic and have then higher tendency to absorb into particles of wastewater (Hai et

al., 2011; Sui et al., 2010; Tadkaew et al., 2011). The sorption of substances to the sludge via adsorption is estimated by the K_d value, being the ratio of the concentration of the substance between the solid and aqueous phase at equilibrium conditions (Li et al., 2015; Vieno and Sillanpää, 2014). A K_d value of 500 L/kg$_{SS}$ is considered to be a limit value for significant removal by sorption (Li et al., 2015; Ternes et al., 2004). The tendency of a substance for biological degradation is estimated by the degradation constant K_{biol}. The biological degradability of substances can be classified by a following way (Joss et al., 2006; Li et al., 2015):

K_{biol} < 0.1 L/g$_{SS}$/d: limited removal by degradation (<20%)
0.1< K_{biol} < 10 L/g$_{SS}$/d: partial removal by degradation (20–90%)
K_{biol} > 10 L/g$_{SS}$/d: efficient removal by biological degradation (>90%)

k_{O3} (M^{-1}s^{-1}) is a rate constant for the reaction of substance such as micropollutant with ozone, higher value indicating more pronounced tendency the react with ozone (Lee et al., 2014). ·OH radical reaction rate of the substance describes the tendency of substance to react with ·OH radicals created during advanced oxidation (Lee et al., 2014; Wols et al., 2013). The pollutants having a high ozone and hydroxyl radical reaction constant are more likely to be degraded during advanced oxidation processes based on ozone and hydroxyl radicals such as pulsed corona discharge.

Table 9　Molecular characteristics of the studied micropollutants. pKa values are given at 25 °C. ·OH radical reaction rates given as L/mol/s are estimated from experiments in purified water. Rate constants for the reaction with ozone (k_{O3}) are given at 20 °C and pH of 7. [a]Unit for K_{biol} of atenolol, metoprolol and sotalol is L/g$_{COD}$/d and [b]unit for K_d of metoprolol and sotalol is L/kg$_{COD}$.

Micropollutant	Classification	Formula	Molecular weight, g/mol	pKa, -	log K_{ow}, -	K_d, L/kg$_{SS}$	K_{biol}, L/g$_{SS}$/d	k_{O3}, M^{-1}s^{-1}	·OH radical reaction rate, L/mol/s
DEET (N,N-diethyl-meta-toluamide)	Pesticide, insect repellent	C$_{12}$H$_{17}$NO	[1]191.3	[2]<2	[1]2.0	-	-	[3]0.126	[4,5]4.95 x 10^9
Paracetamol	Pain killer	C$_8$H$_9$NO$_2$	[1]151.2	[1]9.4	[1]0.46	[6]0.4	[6]106–240	-	-
Ibuprofen	Pain killer	C$_{13}$H$_{18}$O$_2$	[1]206.3	[1]4.9	[1]4.0	[6]7 ± 2	[6]9–22	-	-
Ketoprofen	Pain killer	C$_{16}$H$_{14}$O$_3$	[1]254.3	[1]4.5	[1]3.1	[7]72 ± 111	-	[8]0.4	[9]1.5 x 10^1

Diclofenac	Non-steroidal anti-inflammatory drug	$C_{14}H_{11}Cl_2NO_2$	[1]296.2	[1]4.2	[1]4.5	[6,10,11]16 ± 3	[6,10,11]<<0.1	[12]~1 x 10^6	[9]8.2 x 10^9
Naproxen	Non-steroidal anti-inflammatory drug	$C_{14}H_{14}O_3$	[1]230.3	[1]4.2	[1]3.2	[6,11]10–13	[6]0.4–0.8	-	-
Carbamazepine	Anti-epileptic agent and mood stabilizer	$C_{15}H_{12}N_2O$	[1]236.3	[1]13.9	[1]2.5	[11,13]1.2	[11]<0.01	[12]~3 x 10^5	[9]9.5 x 10^9
Citalopram	Antidepressant and drug for alcoholism	$C_{20}H_{21}FN_2O$	[1]324.4	[14]9.59	[1]3.5	-	-	-	-
Atenolol	Cardioselective beta blocker	$C_{14}H_{22}N_2O_3$	[1]266.3	[1,15]9.6	[1,15]0.16	[7]5.9 ± 4.4	[15,a]0.69	-	-
Bisoprolol	Cardioselective beta blocker	$C_{18}H_{31}NO_4$	[1]325.4	[16]9.4	[1]1.9	-	-	-	[17]3.5 x 10^9
Metoprolol	Selective beta blocker	$C_{15}H_{25}NO_3$	[1]267.4	[15]9.7	[1,15]1.9	[15,b]1	[15,a]0.58	[12]2 x 10^3	[9]8.1 x 10^9
Sotalol	Beta blocker, Beta-antagonist	$C_{12}H_{20}N_2O_3S$	[1]272.4	[18]8.4	[1]0.24	[15,b]37	[15,a]0.29	[12]1.9 x 10^4	[9]7.9 x 10^9
Furosemide	Loop diuretic	$C_{12}H_{11}ClN_2O_5S$	[1]330.7	[1]3.8	[1]2.0	[19]140–160 (Log K_d 2.15–2.2)	-	[12]6.8 x 10^4	[9]1.1 x 10^{10}
Hydrochloro-thiazide	Thiazide diuretic	$C_7H_8ClN_3O_4S_2$	[1]297.7	[1]7.9	[1]-0.07	[7]23.5± 12.6	-	-	-
Trimethoprim	Antibiotic, Dihydrofolate reductase inhibitor antibacterial	$C_{14}H_{18}N_4O_3$	[1]290.3	[1]7.1	[1]0.91	[7,11,20]225–330	[7,11,20]0.05–0.22	-	-
Tetracycline	Antibiotic, Tetracycline-class antimicrobial	$C_{22}H_{24}N_2O_8$	[1]444.4	[1]3.3	[1]-1.4	-	-	-	-
Caffeine	Stimulant for central nervous system	$C_8H_{10}N_4O_2$	[1]194.2	[1]14.0	[1]-0.07	-	-	-	-

Data obtained from: [1](PubChem®, 2019), [2](Yoon et al., 2006), [3](Benitez et al., 2013), [4](Cooper et al., 2010), [5](Abdelmelek et al., 2011), [6](Joss et al., 2006), [7](Radjenović et al., 2009), [8](Real et al., 2009), [9](Wols et al., 2013), [10](Vieno and Sillanpää, 2014), [11](Abegglen et al., 2009), [12](Lee et al., 2014), [13](Li et al., 2015), [14](Huang et al., 2013), [15](Maurer et al., 2007), [16](Li et al., 2012), [17](Nishio et al., 2008), [18](Cabot et al., 2013), [19](Okuda et al., 2009) and [20](Fernandez-Fontaina et al., 2013).

4 Results and discussion

4.1 Micropollutant removal

Enhanced micropollutant removal from various municipal wastewater treatment effluents being MBR permeates, nanofiltration concentrate and synthetic centrate wastewater (simulating the supernatant from the centrifugation of anaerobic digestate after struvite crystallization) with membrane technologies (nanofiltration, reverse osmosis, electrodialysis) and advanced oxidation (pulsed corona discharge) was studied in this work. Aim was to drastically improve the removal of micropollutants and reach over 90% removal rate or ideally removing target pollutants below the analytical detection limits to produce an effluent with minimal concentration of micropollutants.

4.1.1 Tertiary wastewater treatment

Advanced wastewater treatment technologies, namely nanofiltration (NF), reverse osmosis (RO) and pulsed corona discharge (PCD), were studied in this work as a tertiary wastewater treatment to enhance the removal of micropollutants in municipal wastewater treatment as the removal of non-readily biodegradable micropollutants is limited with conventional activated sludge process (CAS) as well as membrane bioreactor processes (MBR) (Table 10). Similar observations on the limited ability of MBR processes to remove non-readily biodegradable micropollutants has been made in several previous studies (Alturki et al., 2010; Dolar et al., 2012; Pathak et al., 2018; Sahar et al., 2011). However, CAS processes as well as MBR processes (MBR, without chemical phosphorus precipitation referred as MBR A, with precipitation referred as MBR B) can remove organic substances measured as COD efficiently, removal rates being 87 (CAS), 91 (MBR A) and 92% (MBR B) in this study (publication II). MBR processes were able to provide more satisfactory nitrogen removal, removal rates being 60% for MBR A and 40% for MBR B compared to 24% obtained by CAS. In addition, the readily biodegradable micropollutants such as pain killers can be efficiently removed in these biological wastewater treatment processes. Removal of studied painkillers was 81– >99% in CAS, 93– >99% in MBR A and 88– >99% in MBR B. However, the removal of some

micropollutants, such as non-readily biodegradable micropollutants diclofenac (K_{biol} <<0.1 L/g_{SS}/d) and carbamazepine (K_{biol} <0.01 L/g_{SS}/d), was modest, since even less than 20% removal rates for these pollutants were obtained by CAS and MBR processes (Table 10). Therefore, nanofiltration (NF), reverse osmosis (RO) and pulsed corona discharge (PCD), were studied in this work to improve the micropollutant removal. The removal efficiencies for micropollutants obtained by NF and PCD in enhanced municipal wastewater treatment are provided in the Table 10.

Table 10   Removal of 17 target micropollutants in CAS and studied process concepts A and B (n=3). Presented removal rates are average values (n=3), range given in brackets, if applicable. Oxidation energy in PCD 0.2 kWh/m3 (single experiment). The average flux in NF270 process 22 L/m^{2}h and the recovery rate 84%. (data from the publication II)

Micropollutant	Influent concentration, µg/L	CAS, %	Concept A		Concept B	
			MBR, %	NF270, %	MBR, %	PCD, %
Paracetamol	36.7(19–54)	>97	>99	>97	>99	>90
Ibuprofen	14.7 (12–17)	>99	>99	>96	98.5 (96.4–99.7)	>90
Ketoprofen	0.64 (0.48–0.76)	75.7 (75–76.3)	90.1 (88.5–92.1)	>88	81.3 (77.1–83.8)	81.5
Naproxen	4.0 (2.0–5.9)	>95	>97	96.3 (95.5–97.1)	90.2 (86.5–94.1)	>94
Caffeine	98.7 (26–160)	99.8 (99.6–99.9)	99.7 (99.6–99.8)	75.8 (52.0–95.0)	99.5 (99.1–99.8)	90.8
Tetracycline	7.9 (2.3–16)	>97	>95	>90	>95	-
Atenolol	0.51 (0.45–0.57)	3.3 (-27–33)	70.8 (56–86)	87.4 (82–94)	69.1 (64–74)	>95.5
Bisoprolol	1.2 (0.94–1.4)	4.8 (-7.7–15)	41.9 (0–65)	90.6 (83–96)	21.7 (0–36)	99.0
Metoprolol	1.9 (1.5–2.2)	19.4 (6.7–33)	18.8 (-6.7–58.6)	84.3 (72–97)	20.1 (0–32)	98.5
Sotalol	0.40 (0.33–0.46)	-37.5 (-42 to -33)	-27.7 (-42 to -13)	84.4 (79–92)	-33.0 (-33.3 to -32.6)	>98.1
Furosemide	16 (8.0–32)	46.5 (33–73)	16.3 (0–38)	95.2 (90–99)	5.6 (-10–34)	>99.2
Hydrochlorothiazide	9.0 (6.1–14)	-22.8 (-57–25)	27.5 (-21–74)	54.7 (50–59)	2.4 (-43–34)	>98.7
Diclofenac	1.6 (1.4–1.7)	19.1 (-41–74)	11.7 (-36–53)	97.4 (96–98)	-24.6 (-47 to -13)	>96.1
Carbamazepine	0.45 (0.39–0.50)	-32.9 (-54 to -12)	-36.4 (-48 to -24)	87.6 (81–95)	-29.8 (-34 to -26)	>99.1
Citalopram	0.34 (0.22–0.46)	27.3 (4.5–47)	24.9 (15–32)	96.6 (95–98)	22.2 (4.5–33)	>94.1
Trimethoprim	0.61 (0.59–0.65)	58.4 (51–73)	8.2 (6.2–10)	88.9 (81–97)	-11.1 (-20 to -3)	>99.8
DEET (N,N-diethyl-meta-toluamide)	0.32 (0.16–0.53)	71.8 (57–88)	94.4 (92–98)	>88.3 (80–95)	93.5 (91–96)	>66.7

In addition to the results presented in the Table 10 above also reverse osmosis with AK (GE Osmonics), BW30 and SW30 membranes (DOW) were utilized in laboratory scale filtration experiment with a DSS Labstak M20 filter to remove target micropollutants from the MBR permeate (process concept B, publication II). Presumably over 96% removal of all 15 target pollutants (ibuprofen, ketoprofen, naproxen, caffeine, atenolol, bisoprolol, metoprolol, sotalol, furosemide, hydrochlorothiazide, diclofenac, carbamazepine, citalopram, trimethoprim and DEET) were observed with the RO membranes. Over 96% removal was measured for all pollutants for which retentions could be determined and other pollutants were removed below detection limits, being 0.005–0.01 µg/L. Very high average pollutant removal rate of 99% was obtained by BW30 and SW30 membranes. In addition to the micropollutants removal also the retention above 95% for conductivity, dissolved organic carbon, total phosphorus and nitrogen was obtained. Over 90% removal or removal below detection limits of 10 target micropollutants, out of 17 target micropollutants studied, such as diclofenac and carbamazepine could be achieved by NF270 nanofiltration (Table 10). PCD oxidation was even more efficient for pollutant removal than the NF. Over 90% removal of all studied micropollutants (Table 10, pollutant concentration below detection limit when retentions presented with < prefix), except ketoprofen (82% removal), was achieved with PCD oxidation and all pollutants were oxidized below 0.1 µg/L concentration with 0.2 kWh/m^3 oxidation energy.

In the case of CAS and MBR processes the removal of micropollutants was mainly dependant on the biodegradability of the pollutant (K_{biol}), but also on the tendency for adsorption in the particles of the sludge (K_d). As can be seen from the Table 10 the pollutants with high biodegradability such as pain killer's paracetamol and ibuprofen were efficiently removed already in the biological processes. Higher sludge retention time (SRT) in the MBR processes further enhanced the removal of biodegradable pollutants. However, with some micropollutants such as sotalol and carbamazepine even negative retentions were obtained in CAS and MBR processes (Table 10). Similar observations for carbamazepine have been made by Li et al., (2015) and Vieno et al., (2007), who also

reported negative retentions in the municipal wastewater treatment with CAS and MBR processes. According to Vieno et al., (2007) the increasing amount of carbamazepine could be explained by the enzymatic cleavage of carbamazepine metabolites in the influent to the parent compound during the CAS process. Similar phenomena could potentially also explain the negative retentions observed for other pollutants in this study (Table 10).

For nanofiltration with NF270 membrane the removal of micropollutants was based on the combined effect of size exclusion, hydrophobicity/hydrophilicity and electrostatic interactions. Utilized NF270 membrane was a hydrophilic membrane (contact angle 30°) with a molecular weight cut-off value (MWCO) of 220–250 Da and membrane is negatively charged at neutral pH area (isoelectric point 2.7) as discussed in the publication II. Therefore, the pollutants having a molecular weight significantly higher than 250 g/mol, such as tetracycline and furosemide, were expected to be retained largely based on size exclusion. However, many pollutants had molecular weight relatively close to NF270 membrane MWCO value or even smaller and in those cases the removal was based mainly on charge repulsion or hydrophilicity/hydrophobicity. This can explain the excellent removal of hydrophobic pollutants such as diclofenac, carbamazepine and furosemide with NF270 membrane, whereas the removal of hydrophilic hydrochlorothiazide and caffeine was clearly lower (Table 9 and 10). In addition to hydrophobicity, also the negative charge of diclofenac and furosemide at feed water pH had an influence on their removal with negatively charged NF270 membrane by charge repulsion. Similar results for the micropollutant removal such as 88% removal of carbamazepine with NF270 membrane have been reported also by Azaïs et al., (2014) and Gur-Reznik et al., (2011), who reported 93 and 92% removal of carbamazepine with NF270 membrane when MBR permeate from municipal wastewater treatment was treated. When looking the target pollutant characteristics (Table 9) and micropollutant removal results (Table 10), the results seems logical in most cases.

However, there are exceptions such as the high removal of paracetamol (>97%) achieved with NF270 membrane (Table 10). Paracetamol is hydrophilic and has a small molecular weight, which is lower than the membrane MWCO and it is not negatively charged at feed pH or neither have a high tendency for adsorption. Therefore, low removal efficiency with high permeability hydrophilic NF270 membrane could be expected. Under 40% removal of paracetamol/acetaminophen with nanofiltration have been also reported by Azaïs et al., (2014) and Chon et al., (2012) and according to Comerton et al., (2007) it does not have strong tendency for adsorption. Therefore, other factors than molecule size, charge, hydrophilicity/hydrophobicity etc. presented in the Table 9 seems to have an effect for the pollutant removal with nanofiltration. Potentially the interactions between paracetamol present in the water and the organic and inorganic impurities in the MBR permeate influences its removal by NF and the geometry and shape of the pollutant may even have an effect to the separation (Azaïs et al., 2014). Based on the results of this study and the target molecule properties it can be concluded that the removal of micropollutants with nanofiltration in municipal wastewater treatment is a very complex issue and it depends on several factors such as membrane and molecule properties, water matrix and the interactions between membrane, molecule and the feed water. Thus, the removal of specific pollutant cannot be purely forecasted based on its properties such as presented in the Table 9.

For reverse osmosis with AK, BW30 and SW30 membranes the same factors can play a role in the removal of micropollutants. However, in the case of these target pollutants (Table 9) the electrostatic interactions and hydrophilicity/hydrophobicity was expected to have smaller influence on the removal as the size exclusion was the dominating separation mechanism. The molecular weight of all target pollutants was above 150 g/mol whereas the MWCO values of the RO membranes can be considered below 100 Da, although usually not characterized by MWCO. Therefore, very high removal with RO membranes (>96%) was achieved in this study. Similar pollutant results with RO treatment of MBR permeate, ultrafiltration (UF) permeate or microfiltration (MF) permeate from municipal wastewater treatment have been reported in other studies (Alturki et al., 2010; Dolar et

al., 2012; Sahar et al., 2011; Sui et al., 2010). For instance, Alturki et al., (2010) achieved over 95% removal of 40 different organic pollutants such as paracetamol, DEET, caffeine, carbamazepine, diclofenac and atenolol, when MBR permeate from municipal wastewater treatment was treated with BW30 (DOW Filmtec) and ESPA2 (Nitto Denko) RO membranes. Similarly Dolar et al., (2012) reported over 99% removal of 20 different micropollutants such as carbamazepine, atenolol, metoprolol and clarithromycin from MBR permeate of municipal wastewater treatment with TR70 RO membrane from Ropur Membranes.

Size exclusion has been identified as the main micropollutant removal mechanism in RO, but also electrostatic interactions and hydrophobic interactions between compounds and RO membrane may play a role in the separation (Alturki et al., 2010; Dolar et al., 2012; Sui et al., 2010). Although the removal of target micropollutants was above 96% in this study for all pollutants, for which the retentions could be calculated, there were small differences in separation as retentions between 96.6 and 99.1% were obtained with the studied RO membranes. The lowest retention, being 96.6%, was measured for hydrochlorothiazide with the AK membrane. As only small differences in the removal rates for different pollutants were obtained within the detection limits of the analysis and very high micropollutant removal overall was achieved the results of this study indicated that size exclusion clearly played the main role in micropollutant removal with RO.

The high efficiency of PCD oxidation for micropollutant degradation (Table 10) was expected as the advanced oxidation with PCD is based on the degradation of organic pollutants with both ozone (O_3, oxidation potential 2.07 V) and hydroxyl radicals ($\cdot OH$, oxidation potential 2.80 V) (publications I, II and IV). The PCD oxidation was very effective; as all pollutants were oxidized below 0.1 µg/L concentration when MBR permeate was treated. This was especially due to stronger presence of non-selective hydroxyl radicals when oxidation was operated at high pulse repetition frequencies (Preis et al., 2013), and strong oxidants efficiently degraded the target pollutants (Table 10). The strong oxidants created in PCD were able to react readily with the target pollutants

present in the MBR permeate as the permeate was virtually solid free and contained only small amount of organics measured as DOC (7.4 mg/L) and COD (18 mg/L). Therefore, the scavenging effect of the water matrix during the advanced oxidation due to effluent organic matter, as also observed by (Katsoyiannis et al., 2011), was very small, and oxidants could readily degrade the target micropollutant already with low oxidation energy of 0.2 kWh/m^3 (publication II).

Similar results for micropollutant degradation with PCD have been obtained by (Ajo et al., 2016; Panorel et al., 2013a, 2013b). Ajo et al., (2016) reported over 95% removal of carbamazepine (initial concentration 5.8 µg/L) from municipal wastewater effluent spiked with pollutants with only 0.3 kWh/m^3 oxidation energy, whereas Panorel et al., (2013a, 2013b) reported complete removal of paracetamol and 80% ibuprofen removal from aqueous pollutant solutions with PCD by using oxidation energy around 2-3 kWh/m^3. The high efficiency of PCD for the degradation of pollutants such as carbamazepine and paracetamol at neutral or acidic environment is mainly due to massive attack of hydroxyl radicals during oxidation (Ajo et al., 2016; Panorel et al., 2013b). However, the ozone can have more significant influence to the degradation if oxidation is conducted at alkaline pH as ozone is more effectively oxidizing the dissociated phenolic moiety of paracetamol (Ajo et al., 2016; Panorel et al., 2013b). Therefore, both ozone and hydroxyl radicals can play a significant role in degradation of pollutants with pulsed corona discharge oxidation and process conditions such as pH, pulse repetition rate and oxygen content as well as pollutant properties determines on which radical plays stronger role in each case (Ajo et al., 2016; Panorel et al., 2013a, 2013b; Preis et al., 2013). In this study the PCD oxidation process conditions such as close to neutral pH, high pulse repetition rate of 840 pps and oxygen rich atmosphere, enhanced the role of hydroxyl radicals in the degradation of target pollutants.

4.1.2 Advanced oxidation of membrane concentrate

The advanced oxidation in the form of pulsed corona discharge (PCD) was very efficient for the micropollutant removal from MBR permeate. Therefore, it was also examined in

this study if PCD oxidation could be an efficient technology to degrade micropollutants in a concentrated water matrix and achieve the 90% removal target. This was done by treating VRF 300 NF concentrate (publication IV) with PCD oxidation (oxidation energy 0–10 kWh/m^3) to remove 9 target pollutants (ketoprofen, bisoprolol, metoprolol, sotalol, furosemide, diclofenac, carbamazepine, citalopram, and DEET). Significant variance was observed in the micropollutant degradation, over 92% degradation was observed for diclofenac, carbamazepine, citalopram and furosemide, whereas the degradation of 82, 51, 33, 44 and 50% was obtained for bisoprolol, sotalol, metoprolol, ketoprofen and DEET at 10 kWh/m^3 oxidation energy (Fig. 9). Thus, the 90% removal target could not be met for all target pollutants when concentrated membrane concentrate was treated by PCD and higher oxidation energy would have been required to meet the target completely. In addition to the micropollutant degradation also the biodegradability of the concentrate was improved as the BOD$_7$/COD ratio could be increased 3.7 times by PCD oxidation. This increase in the BOD$_7$/COD ratio was in a similar level as 1.8–3.5 times increase reported by Lee et al., (2009) in the ozonation of reverse osmosis concentrate (3–10 mg O$_3$/L). Although the biodegradability was significantly improved, the final BOD$_7$/COD ratio of 0.05 was still too low compared to the BOD7/COD ratio of 0.3 which is considered as the limit value between biodegradable and biorefractory (Zhou et al., 2011). Higher oxidation energy would have been required to make the concentrate readily biodegradable and enable its recirculation back to the biological wastewater treatment process.
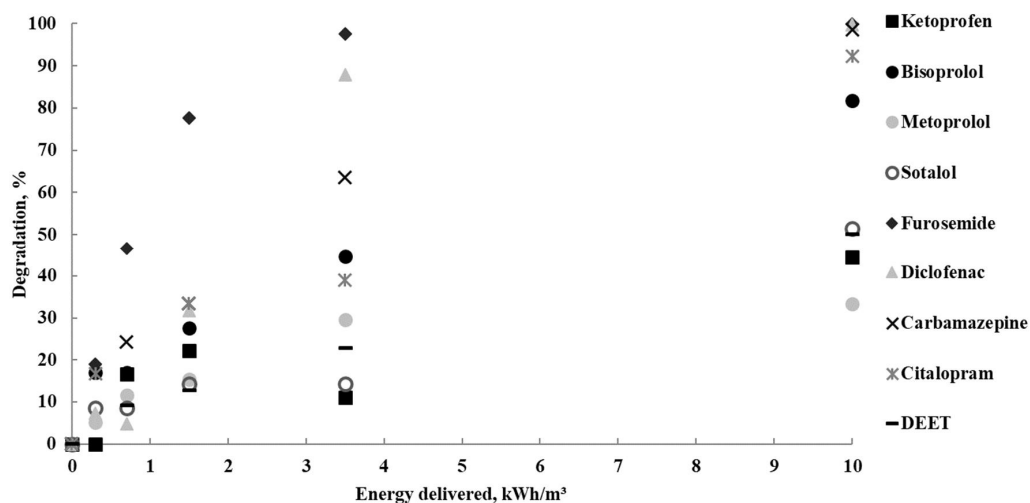
Fig. 9   Degradation of target pollutants in the pulsed corona discharge (pulse repetition frequency 840 pps) oxidation of VRF 300 nanofiltration concentrate (pH 5.9, conductivity 12 670 µS/cm, COD 5930 mg/L). (data from publication IV)

Regression analysis (described in the section 3.5) was conducted to identify the main parameters for the degradation of micropollutants in the PCD oxidation of NF concentrate. Analysis concluded that the molecular weight of the molecule, the amount of double bonds in the molecule structure and ·OH degradation constant were the three main parameters having an effect for the degradation. Other parameters included to the regression analysis, being ozone reaction constant k_{O3}, pKa value of the molecule and Log K_{ow} value of the molecule, had only minor effect to the degradation. All three main parameters had a positive correlation, meaning that bigger the value of the parameter the better degradation. These three parameters explained 96% of the variation of degradation rate of micropollutants, molecular weight being the most significant parameter (53% of the variation). Degradation of pollutants were concluded to be more dependent on the hydroxyl radicals created in PCD than from the ozone in this study. To re-enforce this observation and to see the effect of water matrix to the oxidation a corresponding regression analysis was conducted with the data from the MBR permeate oxidation. Results of this analysis were very similar, same three parameters (molecular weight, amount of double bonds and ·OH degradation constant) were the main parameters

influencing the degradation of micropollutants (over 99% of the variation, molecular weight 47%).

According to these results the micropollutants will oxidize more readily in the PCD oxidation if they have a large molecular weight, contains multiple double bonds in their structure and have a large $\cdot OH$ degradation constant, such as furosemide (Table 9, Fig. 9), over to smaller molecules with more recalcitrant nature toward hydroxyl radicals, such as ketoprofen and DEET (Table 9, Fig. 9). Furthermore, ozone plays smaller role in oxidation compared to the hydroxyl radicals under present process conditions. The high pulse repetition frequency (840 pps) utilized in this study presumably increased the influence of hydroxyl radicals over ozone to the degradation as also observed by (Preis et al., 2013). In earlier studies concerning micropollutant degradation with PCD especially the role of hydroxyl radicals and also ozone as main factors for the degradation has been highlighted (Ajo et al., 2016; Dobrin et al., 2013; Panorel et al., 2013a, 2013b). The effect of double bonds amount in molecule structure to the degradation have been discussed in only limited studies (Ajo et al., 2016). Therefore, this study gives new insights concerning the determining factors for micropollutant degradation during PCD oxidation by highlighting the role of molecular weight and amount of double bonds within molecule structure for the degradation in addition to the role of strong radical's hydroxyl radical and ozone.

The oxidation results with the NF270 concentrate were very different compared to the ones with MBR permeate (Table 10) and significantly, more variance in the oxidation rates were observed. This was expected as the concentrate studied contained high concentration of organics (DOC 2130 mg/L, COD 5930 mg/L), which led to significant scavenging effect of the water matrix. Thus, significant amount of oxidation energy was spent, and radicals consumed, for the oxidation of effluent organic matter. Therefore, differences in the oxidation rates of target micropollutants came more visible and the 90% removal target was not reached for all pollutants.

Some pollutants such as furosemide, diclofenac and carbamazepine had very high hydroxyl radical and ozone reaction rate constants enabling their efficient degradation also in the concentrated water matrix. Out of these three pollutants furosemide and diclofenac also had one of the highest molecular weights out of the 9 studied pollutants (Table 9), but carbamazepine had second smallest molecular weight from the studied pollutants and yet high removal for carbamazepine was obtained in PCD. Similarly when looking the pollutant properties (Table 9) overall for furosemide and ketoprofen it is quite logical that furosemide is readily degradable (high molecular weight and very high hydroxyl radical reaction rate) whereas ketoprofen with small molecular weight, small hydroxyl radical and ozone reaction constant is not readily degraded from NF concentrate with PCD. However, after these two pollutants the actual oxidation results (Fig. 9) for other pollutants are not directly in line with the pollutant properties (Table 9). Therefore, single pollutant characteristic, such as hydroxyl degradation reaction rate, cannot be used to forecast degradation behaviour in the PCD oxidation. This means that the degradation of micropollutants studied during PCD oxidation is more complex issue, which depends on several pollutant properties as well as from the water matrix and oxidation process conditions.

4.1.3 Micropollutant transport during electrodialysis

Laboratory scale electrodialysis equipped with five cation exchange membranes (General Electric CR67) and four anion exchange membranes (General Electric AR204SZRA) was used to treat synthetic centrate wastewater (Table 2, section 3.1) and to study if pharmaceuticals can migrate through the ion exchange membranes to the concentrate product. According to the results less than 8% from the pollutants present in the dilute feed solutions were transported to the final concentrate product in the ED treatments conducted (Table 11). Thus, over 92% retention of all target pollutants, when calculated as a percentage of the feed micropollutant amount (µg) retained by the ion exchange membranes, was achieved in the ED experiments. However, significant micropollutant concentrations were still measured in the final concentrate product for some pollutants such as atenolol and metoprolol as presented in the Table 12. The results indicated that

atenolol and metoprolol were either accumulating to the final concentrate product, meaning that the pollutant concentration µg/L was higher in the final product than in the initial feed, or proportioning, meaning that the pollutant split between product and diluent compartments due to hydraulic changes including osmotic transfer to concentrate. Trimethoprim and hydrochlorothiazide were proportioning according to results, whereas other pollutants were retained by the ED membranes (Table 12).

Table 11   Average percentage of the target pollutants transported from the dilute feed solution to the final concentrate product in the 8 h ED treatments with laboratory scale ED unit. (n=3, 95% confidence interval given in brackets). Data from the publication VI.

Percentage of pollutant in the final product from the initial feed, %			
Pollutant	Treatment 1 (10 µg/L)	Treatment 2 (10 µg/L)	Treatment 3 (100 µg/L + strong initial product)
Caffeine	0.57 (0.08)	0.45 (0.03)	0.49 (0.03)
Carbamazepine	0.32 (0.33)	0.22 (0.21)	0.17 (0.08)
Atenolol	5.3 (5.6)	6.5 (5.2)	2.9 (0.9)
Metoprolol	2.0 (2.4)	2.2 (1.7)	7.4 (1.1)
Trimethoprim	1.6 (1.9)	1.2 (1.8)	0.4 (0.4)
Diclofenac	0.04 (0.05)	0.01 (0.01)	0.00053 (0.0006)
Ibuprofen	0.04 (0.006)	0.004 (0.0007)	0.004 (0.008)
Furosemide	0.06 (0.003)	0.0059 (0.0001)	0.009 (0.006)
Hydrochlorothiazide	1.9 (2.2)	1.7 (1.3)	0.7 (0.3)

Table 12   Average (n=3) micropollutant concentrations (µg/L) in feed solutions and final concentrate products during different ED treatments. Treatment 1 corresponds to a 8h ED treatment with a feed micropollutant concentration 10 µg/L, treatment 2 corresponds to a 8h ED treatment with a feed micropollutant concentration 100 µg/L and treatment 3 is the 8h ED treatment with a feed micropollutant concentration 100 µg/L and strong initial feed (around 7 times higher concentration of ions compared to initial feed). Data from the publication VI.

	Micropollutant								
	Caffeine	Carbamaze-pine	Atenolol	Metoprolol	Trimetho-prim	Diclofenac	Ibuprofen	Furosemide	Hydrochloro-thiazide
Treatment 1									
Feed, µg/L	10.5	12.2	10.1	10.4	10.0	11.3	10.5	11.0	11.7
Product, µg/L	1.2	0.87	10.6	4.3	3.3	0.1	0.09	0.13	4.5
Treatment 2									
Feed, µg/L	99.8	115.0	100.6	93.6	90.7	109.3	107.9	112.3	123.0
Product, µg/L	9.2	4.9	143.7	43.1	21.6	0.22	0.08	0.14	39.2
Treatment 3									
Feed, µg/L	103.0	98.3	147.0	104.0	109.7	106.7	97.4	102.6	109.7
Product, µg/L	9.3	3.1	78.7	139.3	9.3	0.01	0.08	0.17	13.2

According to these results (Tables 11 and 12 and publication VI) the hydrophobicity/hydrophilicity had a strong influence on the micropollutant transport through the ED membranes, but also the charge influenced the transport. The fact that some transport of both positively and negatively charged pollutants was observed meant that transport both across the anion and cation exchange membranes occurred during ED experiments. This highlighted the influence of molecule hydrophobicity/hydrophilicity to the transport of target pollutants. Pollutants having a high hydrophobicity and negative charge (at pH 8) such as diclofenac and ibuprofen were preferentially retained by ion exchange membranes. Similar conclusions has been drawn by Pronk et al., (2006), who studied the removal of micropollutants from anthropogenic urine with ED. They concluded that the removal of micropollutants with ED was determined by adsorption, which was effected highly by molecule hydrophobicity/hydrophilicity as well as electrostatic interactions but also by diffusion and sieving effects (Pronk et al., 2006). However, in this dissertation study the sieving and diffusion did not seem to have as major role in the micropollutant removal with ED according to the results and target pollutant properties. The pollutant molecule size did not have a clear effect to the transport through ion exchange membranes. Similar observations about removal mechanisms were also made in the nanofiltration with NF270 membrane (publication II, section 4.1.1) as also the removal of micropollutants with NF270 membrane was mainly depending on hydrophobicity/hydrophilicity and electrostatic interactions in addition to size exclusion. Thus, this study indicates that some similar separation mechanisms play a role in micropollutant removal in both nanofiltration and electrodialysis.

When considering the suitability of the concentrate product for fertilizer applications, it needs to be noted that the concentrations of the target pollutants studied are expected to be lower in the real municipal wastewater effluents compared to these synthetic wastewaters studied. Also, for the application of the concentrate product as liquid fertilizer the dose of concentrate product in respect to the irrigation water would be low. However, further long-term ED studies with real wastewaters are required to confirm the observations of this study and to examine if ED can also retain other micropollutants

present in the real municipal wastewaters to enable production of a concentrate product suitable for fertilizer applications.

4.1.4   Technology comparison for micropollutant removal

Two pressure driven membrane technologies (NF and RO), one membrane technology driven by electrical potential difference (ED) and one advanced oxidation process based on non-thermal plasma (PCD) were examined in this work for the micropollutant removal from municipal wastewaters. As the studied technologies had very different mechanisms of operation, also the micropollutant removal results varied between the studied technologies (Table 13).

Table 13   Average removal of 17 target micropollutants with different technologies studied in this work. Range given in brackets, if applicable. Feed effluents presented in section 3.1. Pollutant concentration below detection limit when retentions presented with > prefix. Micropollutant removal in electrodialysis were calculated from the average concentration differences between feed solutions and final concentrate products across 3 different electrodialysis treatments (n=3 for each treatment).

| | Removal efficiency, % | | | | |
Micropollutant	Nanofiltration (NF270 membrane, feed MBR permeate A)	Reverse osmosis (SW30 membrane, feed MBR permeate B)	Electrodialysis (feed synthetic centrate wastewater)	Pulsed corona discharge (PCD, feed MBR permeate B)	Pulsed corona discharge (PCD, feed NF270 concentrate)
Paracetamol	>97	-	-	>90	-
Ibuprofen	>96	>60	99.6 (99.1–99.9)	>90	-
Ketoprofen	>88	>98	-	81.5	44
Naproxen	96.3 (95.5–97.1)	>98	-	>94	-
Caffeine	75.8 (52.0–95.0)	>97	90.1 (88.5–91.0)	90.8	-
Tetracycline	>90	-	-	-	-
Atenolol	87.4 (82–94)	>94	-0.3 (-42.8–46.4)	>95.5	-
Bisoprolol	90.6 (83–96)	98.8	-	99.0	82
Metoprolol	84.3 (72–97)	98.6	26.3 (-33.9–58.8)	98.5	33
Sotalol	84.4 (79–92)	>98	-	>98.1	51
Furosemide	95.2 (90–99)	>99	99.5 (98.8–99.9)	>99.2	>99.9

Hydrochlorothiazide	54.7 (50–59)	98.4	72.5 (61.3–88.0)	>98.7	-
Diclofenac	97.4 (96–98)	98.8	99.6 (99.1–99.99)	>96.1	99.7
Carbamazepine	87.6 (81–95)	99.1	95.2 (92.9–96.8)	>99.1	>98.5
Citalopram	96.6 (95–98)	>96	-	>94.1	92.2
Trimethoprim	88.9 (81–97)	99	78.2 (67.0–91.5)	>99.8	-
DEET (N,N-diethyl-meta-toluamide)	>88.3 (80–95)	>80	-	>66.7	50

The best results overall for micropollutant removal was achieved with reverse osmosis and pulsed corona discharge oxidation (Table 13). Both technologies achieved on average above 95% removal of target pollutants, when MBR permeate was treated. Also, electrodialysis excluded most of the target micropollutants, such as diclofenac, carbamazepine, ibuprofen and furosemide, efficiently from the concentrate product (Table 13, publication VI), retentions being on average over 95% for these pollutants. But, even accumulation of atenolol and metoprolol to the concentrate product was observed in some experiments as for instance the average concentrations of 10.6 µg/L for atenolol in the final concentrate product was measured in the lab scale ED experiments with the synthetic wastewater feed having a micropollutant concentration of 10 µg/L (Table 12). However, as very nutrient rich concentrate product (NH_4^+-N 7.1 g/L and K^+ 2.5 g/L) was achieved in the publication V with pilot scale ED of real centrate wastewater, a large dilutions of the concentrate product would be required for a real application as a liquid fertilizer. This is because the liquid fertilizers can often contain only around 0.33-3.3 g/L of total nitrogen and less than 0.1 g/L of NH_4^+-N (Martínez-Alcántara et al., 2016; Phibunwatthanawong and Riddech, 2019). This kind of dilution would significantly reduce the concentration of ammonia and micropollutants for application purposes.

When considering the applicability of utilized technologies for municipal wastewater treatment the electrodialysis can be used mainly as a specific technology for nutrient concentration and recovery. Nanofiltration, reverse osmosis and pulsed corona discharge

on the other hand can be used as a tertiary polishing treatment. These processes further enhance the effluent quality after traditional activated sludge process or MBR process by removing or degrading micropollutants and removing also other organic compounds (also inorganic compounds in case of membrane technology). Furthermore, tertiary membrane filtration can be also utilized for nutrient, such as phosphorus, concentration and recovery (publication III).

Electrodialysis can be very energy efficient technology for nutrient recovery in anaerobic wastewater treatment as even smaller energy consumption for NH_4^+-N recovery can be achieved with ED (4.9 kWh/kg NH_4^+-N in ED, publication V) than in the traditional nitrogen recovery technologies such as Haber-Bosch process for nitrogen fertilizer production (6.2 kWh/kg of N in Schaubroeck et al., (2015), 7.8 kWh/kg of NH_3 in Paschkewitz, (2012) and 10.3 kWh/kg of N in Maurer et al., (2003)). If the aim is only to enhance the micropollutant removal, then PCD oxidation can be very energy efficient alternative as it was able to degrade all target pollutants below 0.1 µg/L, when MBR permeate was oxidized with an energy consumption of 0.2 kWh/m^3.

The formation of harmful oxidation by-products such as trihalomethanes is often considered as a major challenge when applying advanced oxidation in wastewater treatment (publication I). The fact that complete mineralization was not achieved in this work in the PCD research conducted (publication II, publication IV) indicates that some oxidation by-products was formed. According to literature the final oxidation by-products forming during PCD oxidation of wastewaters containing organic micropollutants are mainly carboxylic acids such as acetic, formic and oxalic acid (publication IV, (Dobrin et al., 2013; Panorel et al., 2013a, 2013b)). Although the final oxidation products in PCD oxidation seems to be small molecular weight substances such as carboxylic acids, the formation and exact content of the oxidation by-products probably needs to be confirmed in detail in future research with real wastewaters before applying PCD oxidation in full scale for municipal wastewater treatment applications.

For the removal of both organic micropollutants as well as the removal of DOC and COD as well as the nutrient separation and concentration the membrane technologies NF and RO are more suitable. RO can offer very high efficiency for the removal of micropollutants (Table 13), but the energy consumption on average is expected to be significantly higher (>1.5 kWh/m^3, (Bellona et al., 2012; Fritzmann et al., 2007)) than the estimated energy consumption for NF270 nanofiltration process (0.8–0.9 kWh/m^3, (Bellona et al., 2012)) as discussed in the publication II. Also, the permeabilities in nanofiltration, especially when using high permeability NF270 membrane, are higher than in the reverse osmosis, which leads to smaller membrane area requirements and consequently to smaller capital and operational costs. Therefore, the NF can be often more desirable membrane technology if it can offer high, ideally above 90%, removal efficiency for micropollutants.

4.2   Nutrient recovery

Nutrient recovery in this dissertation work was studied by two different processes, being two-stage nanofiltration process for concentration of phosphorus and precipitation of calcium phosphate and concentration of nutrient ions by electrodialysis to produce a liquid fertilizer product. The target was to focus on technologies which could be able to concentrate and recover nutrients without addition of chemicals.

4.2.1   Calcium phosphate recovery from membrane concentrate

Phosphate recovery as a calcium phosphate was examined in this study with a two stage NF270 nanofiltration where the amount of membrane concentrate was minimized and simultaneously calcium phosphate precipitated spontaneously. A very high VRF value of 300 (0.3% of the initial feed volume) could be obtained by two stage NF270 nanofiltration, final concentration stage being shear enhanced membrane filtration in a cross rotational CR350 filter. Average permeability of 8.9 L/(m^{2}hbar) could be maintained during concentration filtration in the CR350 filter. The CR350 filter has rotating rotors (13.7 m/s tip speed) which create very high turbulence on the membrane surface and prevent membrane scaling. Based on the results the phosphorus started to

precipitate as calcium phosphate (hydroxyapatite, HAP) between VRF 20 and 50 (after VRF 50 the phosphorus and calcium concentrations did not increase linearly). This spontaneous precipitation as HAP (80% purity according to EDS analysis, Fig. 10) enabled about 52% phosphorus recovery as a solid phosphate product based on phosphorus and calcium mass balances. Approximately 86% of the phosphorus could be recovered in total in this non-optimized treatment concept either as a precipitate (HAP, purity ~ 80%, 52% of the P_{tot}) or in the concentrated liquid (34% of the P_{tot} in the membrane concentrate). Thus, with this process concept it was possible to recover nutrients as a form of calcium phosphate without addition of precipitation chemicals and the concentration filtration could be carried out without significant membrane fouling.

EDS analysis	
Element	Wt %
O	40.3
Ca	28.5
P	14.9
C	12.9
Mn	0.9
S	0.9
Mg	0.7
Fe	0.7
Na	0.3
Al	0.2
Total	100

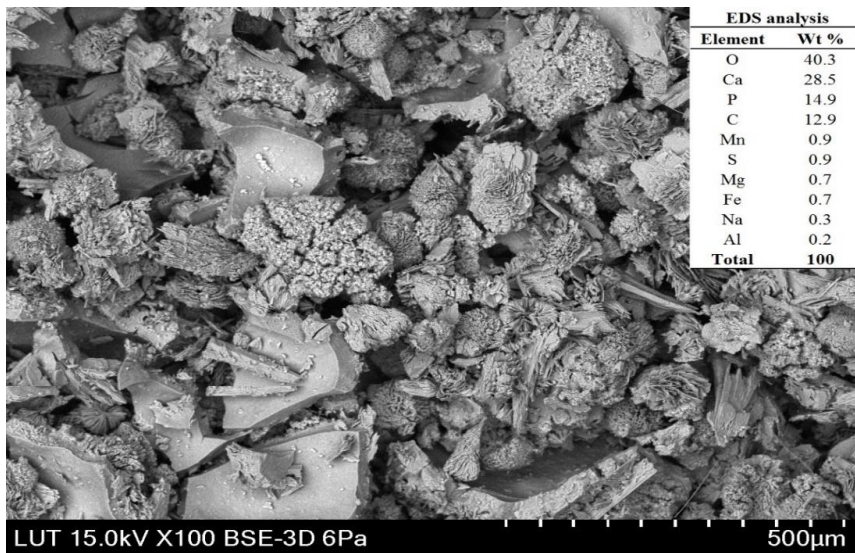LUT 15.0kV X100 BSE-3D 6Pa   500µm

Fig. 10 Scanning electron microscope (SEM) image and EDS analysis of the precipitate formed during second stage filtration of NF270 concentrate with CR350 filter. Hitachi SU3500 scanning electron microscope, BSE detector, 15 kV acceleration voltage. Thermo Scientific UltraDry SDD EDS energy dispersive X-ray spectroscopy, dual detector, 1.5 X 1mm spot size, Pathfinder software. Calcium phosphate precipitates present in the figure as ´rosaceous structures´ (RS). (publication III)

The obtained phosphorus recovery rate (52%) was low when compared to 65–80% obtained by a commercial scale Crystalactor® process, which has been used for phosphorus recovery in municipal wastewater treatment (Desmidt et al., 2015; Giesen, 1999; Woods et al., 1999). Crystalactor® process is based on fluid-bed type crystallizer

which generates phosphate crystal pellets from phosphorus rich wastewater at elevated pH, usually between 8.5-9.5. However, the process is complex and requires carbon dioxide stripping, high operational pH for efficient crystallization and capital costs are often high. (Desmidt et al., 2015; Giesen, 1999) Although the achieved phosphorus recovery rate in this two-stage nanofiltration process was only moderate (52%), the process was not yet completely optimized for phosphorus recovery. With further research work such as optimization of calcium phosphate precipitation process (longer residence times, possible pH adjustment, modification of precipitation tank geometry etc.) the efficiency and feasibility of the process can be potentially improved significantly.

4.2.2 Nutrient recovery with electrodialysis

A Pilot-scale electrodialysis unit (ED) utilizing cation exchange membranes (General Electric CR67) and anion exchange membranes (General Electric AR204SZRA) was used to recover elemental nutrients from real centrate wastewater (section 3.2, publication V). Experimental results demonstrated that a highly concentrated product rich in NH_4^+-N (7.1 g/L) and K^+ (2.5 g/L), with a potential use as liquid fertilizer, could be achieved in ED (Fig. 11) by concentrating nutrient ions from the centrate wastewater feed stream (NH_4^+-N 0.81 g/L, K^+ 0.22 g/L) to the concentrate product stream via continuous 72 h electrodialysis process under constant current of 2.5 A (20 A/m^2). Continuous ED process was operated without significant fouling problems. Only one cleaning of the ED cell with 0.5% NaOCl for 2h followed by recirculation of 1% HCl solution overnight was conducted after each 72h trial.
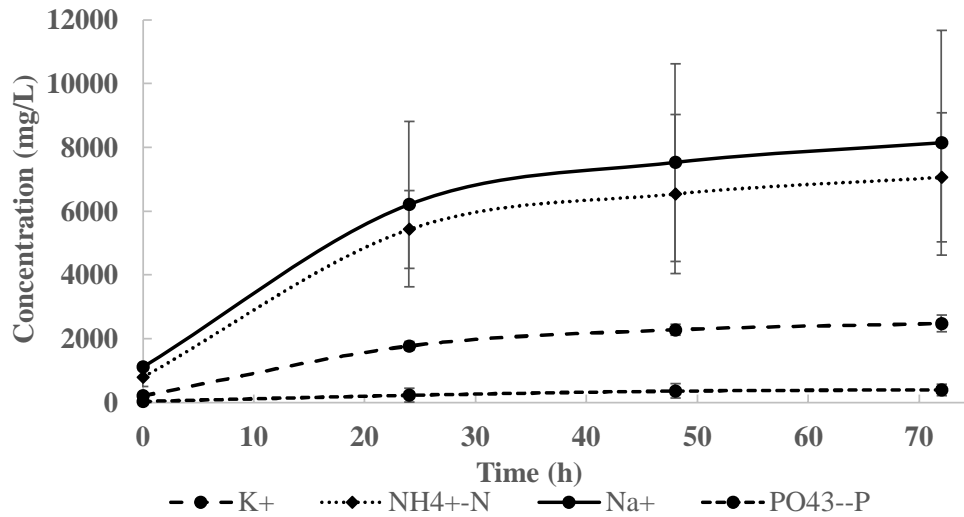
Fig. 11   Concentration of major cations K^+, NH_4^+-N, Na^+ and PO_4^{3-}-P in the concentrate product over the experimental duration in pilot scale electrodialysis treatment of centrate wastewater ((n=3). Error bars = 95% confidence interval. (publication V)

This concentration of ammonia nitrogen corresponded to an average concentration factor (mg/L) of 8.77 times (8.31 on a molar basis) which was in a similar range as over 7 and 6.67 times NH_4^+-N up-concentration achieved by Ippersiel et al., (2012) and Zhang et al., (2013) with electrodialysis. Average current efficiency used to transport ions was approximately 75% during ED experiments. Also, the energy efficiency of the pilot scale electrodialysis was very promising as discussed before in this study, the power required to produce 1 kg of NH_4^+-N was calculated to be only 4.91 ± 1.47 kWh/kg (excluding pumping energy). This energy consumption was significantly lower compared to >7.5 kWh/kg reported for the commercial Haber-Bosch process (Maurer et al., 2003; Paschkewitz, 2012).

As the electrodialysis was able to produce highly concentrated product energy efficiently without major membrane fouling and exclude pharmaceuticals effectively (publication VI) the technology proved to be very promising method to concentrate nutrients and create liquid fertilizer product. However, further research with real wastewaters is required to optimize the product recovery, determine the optimal performance under long

term operation, investigate the possible micropollutant transport in the real wastewater matrix and further optimize the energy consumption.

Thus, both two stage nanofiltration process and pilot scale electrodialysis were able to efficiently concentrate and recover nutrients without a need for the addition of precipitation chemicals and only minor membrane fouling was observed during these membrane treatments. The potential of these technologies for value component recovery in municipal wastewater treatment was also highlighted in the publication I, where both shear enhanced nanofiltration or reverse osmosis and electrodialysis were identified as potential technologies for nutrient concentration.

5   Conclusions and recommendations for future research

Depletion of natural resources such as fresh water and phosphate creates pressure to pursue towards resource recovery in municipal wastewater treatment. Requirements for environmental protection are constantly increasing, leading towards more stringent discharge limits in wastewater treatment plants. In addition, the aquatic environment is under constant stress due to eutrophication, but also due to increasing presence of harmful micropollutants, such as pharmaceuticals, hormones and pesticides, in the aquatic environment. Conventional activated sludge processes, traditionally used for municipal wastewater treatment, are not designed for micropollutant removal and especially partially biodegradable micropollutants are poorly removed. Advanced treatment technologies are required to tackle these two mega trends in wastewater treatment.

Therefore, the aim of this thesis was to examine selected advanced wastewater treatment technologies for enhanced removal of target micropollutants and nutrient recovery in municipal wastewater treatment by focusing on mature technologies as well as emerging technologies minimizing the use of chemicals. Target in this study was the be able to remove over 90% of target micropollutants with the studied technologies and examine if nutrients could be concentrated and recovered efficiently with the studied technologies without addition of precipitation chemicals and significant membrane fouling. This study aimed to identify the removal mechanisms for target micropollutants in each studied technology and examine if pollutant removal could be predicted based on the molecule characteristics.

Nanofiltration, reverse osmosis and pulsed corona discharge oxidation were studied as a post-treatment of municipal wastewater treatment (after membrane bioreactor process) mainly to enhance micropollutant removal. Good results were obtained, removal rates above 84% with nanofiltration, over 90% with pulsed corona discharge oxidation and over 96% with reverse osmosis were achieved for most target pollutants, such as diclofenac, carbamazepine and furosemide, studied in this work. Oxidation proved to be

very promising technology for micropollutant degradation from MBR permeate as all target pollutants could be degraded below 0.1 µg/L concentration with only 0.2 kWh/m^3 oxidation energy. More variable results for micropollutant degradation were obtained when PCD oxidation was conducted in a concentrated water matrix of NF270 concentrate with a VRF of 300. Over 92% degradation with oxidation energy of 10 kWh/m^3 was observed for diclofenac, carbamazepine, citalopram and furosemide, whereas the degradation of 82, 51, 33, 44 and 50% was obtained for bisoprolol, sotalol, metoprolol, ketoprofen and DEET. Ion exchange membranes were also able to retain most pharmaceuticals very efficiently in the laboratory scale electrodialysis study with synthetic wastewater as over 95% retention of target pollutants diclofenac, carbamazepine, ibuprofen and furosemide was achieved.

The selection of the technology depends on the treatment target. Reverse osmosis provided the best results overall for both micropollutants as well as COD, DOC and phosphorus removal. However, it was the most energy intensive process out of studied processes. Therefore, nanofiltration with NF270 membrane could be the chosen technology in applications where both enhanced removal of micropollutants as well as COD, DOC and phosphorus, such as >95% removal achieved in this study, is required. This providing that enough barrier for micropollutants, ideally over 90% removal, is reached. Pulsed corona discharge oxidation on the other hand is the most promising technology when only enhanced micropollutant degradation from MBR permeate or similar dilute effluent is required.

The removal of micropollutants with NF270 membrane was observed to be due to the combined effect of size exclusion, hydrophobicity/hydrophilicity and electrostatic interactions whereas the removal of micropollutants with reverse osmosis was mainly due to size exclusion. Based on the oxidation results, pollutant properties and regression analyses conducted the molecular weight of the molecule, the amount of double bonds in the molecule structure and ·OH degradation constant were the main parameters having an effect for the micropollutant degradation during PCD oxidations conducted in this study.

In electrodialysis the molecule hydrophobicity/hydrophilicity had a strong influence on the micropollutant transport through the ion exchange membranes and the charge also influenced the transport whereas the sieving and diffusion did not seem to have as major role according to the results and target pollutant properties. Overall the results of this study indicate that the removal of specific pollutant with the studied technologies cannot be purely forecasted based on single pollutant parameter such as molecular weight, pKa value, log K_{ow} value and $\cdot$OH degradation constant, and therefore experimental data is also required. This is because the removal of micropollutants in each of the studied technologies seem to be a result of an interaction of several pollutant properties, water matrix and process specific conditions such as membrane characteristics in membrane processes and pulse repetition rate as well as oxygen content in the pulsed corona discharge oxidation.

Nutrient recovery was examined with two different membrane processes, being two-stage nanofiltration (NF270 membrane) including shear-enhanced nanofiltration for phosphorus concentration and recovery and electrodialysis for the concentration of nutrient ions NH_4^+-N and K^+. Nanofiltration process with 2.5" spiral wound module for filtration of MBR permeate up to VRF 6 followed by shear enhanced nanofiltration with CR350 filter was able to reach very high VRF value of 300 (average permeability 8.9 L/(m^{2}hbar)) and thus efficiently minimize the amount of membrane concentrate with minor membrane fouling. Phosphorus was simultaneously concentrated and spontaneously precipitated in a separate settling tank as a calcium phosphate (hydroxyapatite, 80% purity) with a recovery rate of 52%. Thus, nutrients could be efficiently recovered with the two stage nanofiltration process without addition of precipitation chemicals.

Experimental results showed that continuous pilot scale electrodialysis was able to produce highly concentrated fertiliser product rich in NH_4^+-N (7.1 g/L) and K^+ (2.5 g/L) (potential use as liquid fertilizer) by concentrating nutrient ions from real centrate wastewater (NH_4^+-N 0.81 g/L, K^+ 0.22 g/L) to the concentrate product. Electrodialysis

was operated without significant fouling problems, as only one cleaning of the ED cell was done after each 72h trial. The power required to produce 1 kg of NH_4^+-N in electrodialysis was calculated to be only 4.91 ± 1.47 kWh/kg (excluding pumping), which was lower than commercial Haber-Bosch process producing ammonia (7.8–10.3 kWh/kg). This study indicates that the concentrate product produced energy-efficiently by ED could be utilized safely as liquid fertilizer, especially since a dilution of the concentrate product for fertilizer purposes is required further reducing the micropollutant concentrations in the product. Thus, both two stage nanofiltration and electrodialysis proved to be potential technologies for nutrient concentration and recovery in this work. Similar observations were made also in the publication I, which highlighted the potential of these technologies for the value component recovery from the membrane concentrates of municipal wastewater treatment.

Even though the presented results related to the removal of micropollutants and nutrient recovery are promising, however, some further research is recommended to validate the results of this work. To validate and confirm the findings of this study concerning micropollutant removal, but also in general to examine fouling in these membrane processes, some long-term pilot scale experiments with real wastewater effluents could be executed by using the process concepts studied including nanofiltration and pulsed corona discharge oxidation. The formation and composition of oxidation by-products during the pulsed corona discharge oxidation of municipal wastewater treatment effluents, such as ones studied in this work, should be also examined in detail to confirm the safety of the treated effluents.

When concerning the further research needs arising from the nutrient recovery experiments with the two-stage nanofiltration process presented in this study it is evident that some optimization of the calcium phosphate precipitation process (longer residence times, possible pH adjustment, modification of settling tank etc.) could be executed in order to evaluate the process feasibility and its scale-up potential in detail. Further electrodialysis research with real wastewaters would be beneficial based on the results of

this study in order to optimize the product recovery, long-term performance and the energy consumption in continuous electrodialysis process as well as to investigate the possible micropollutant transport in the real water matrix. Also, in general further research data is required from the potential micropollutant transport during electrodialysis treatment of different real nutrient rich wastewaters to confirm the suitability of concentrated nutrient products for liquid fertilizer use. This kind of future research would help to scale-up studied technologies and process concepts for full scale applications, when appropriate.

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Publication I

Kimmo Arola, Bart Van der Bruggen, Mika Mänttäri, and Mari Kallioinen
Treatment options for nanofiltration and reverse osmosis concentrates from municipal wastewater treatment: A review

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Treatment options for nanofiltration and reverse osmosis concentrates from municipal wastewater treatment: A review

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ABSTRACT

Conventionally treated municipal wastewaters create environmental challenges due to eutrophication of effluent receiving waters and significant concentrations of micropollutants and other harmful impurities. To enhance purification, different tertiary membrane filtration technologies are utilized. The concentrate produced in membrane filtration is a voluminous waste stream, which further treatment is challenging. Also the valuable components in the concentrate remain typically unutilized. This review identifies potential treatment strategies for membrane concentrates originating from municipal wastewater treatment and evaluates approaches for value component recovery and waste minimization. Various technologies were examined as possible options for advanced concentrate treatment. Study concluded that electrodialysis processes or shear enhanced nanofiltration or reverse osmosis could be promising approaches to concentrate the valuable components, mainly nutrients, in concentrate. Few technologies were seen potential for value component recovery. These included ammonium recovery or struvite recovery with electrodialysis combined with crystallization or with struvite crystallization as well as calcium phosphate recovery with EPR process or with combined process of electrodialysis and crystallization. The concentrate recirculation back to the biological treatment can be enabled by concentrate oxidation which increases biodegradability. Combining these unit processes appropriately, an efficient strategy of membrane concentrate management can be implemented and even zero wastewater discharge achieved.

1. Introduction

Depleting natural resources such as fresh water and phosphate minerals and the requirements to improve protection of the environment are increasingly leading towards more stringent legislative restrictions on

discharges from wastewater treatment plants (WWTPs). Membrane filtration such as nanofiltration (NF) or reverse osmosis (RO) as a tertiary treatment improves significantly the quality of chemically and biologically treated municipal wastewaters. NF and RO processes enable the production of highly purified water as form of permeate from municipal wastewater and potentially even the recovery of nutrients. However, in addition to the purified permeate stream, these processes produce a membrane concentrate that is a concentrated wastewater stream potentially rich in nutrients, salts, micro-organisms and refractory organic compounds. From both an environmental point and resource efficiency point of view, membrane concentrate treatment is a significant part of membrane based wastewater purification.

Regulations and alternatives for membrane concentrate disposal have been comprehensively studied in earlier reviews by Pamela, Smith, and Mohamed (2009) and Van der Bruggen, Lejon, and Vandecasteele (2003). According to Van der Bruggen et al. (2003), traditional membrane concentrate disposal options are: direct or indirect discharge to surface or ground water and discharge to landfill or incineration, while more desirable option is recovery of valuable substances from the membrane concentrates before disposal of the concentrate. Treatment and disposal options for membrane concentrates, mainly reverse osmosis, from desalination plants have been examined in earlier reviews by Afrasiabi and Shahbazali (2011); Khan, Murchland, Rhodes, and Waite (2009); Kim (2011); Neilly, Jegatheesan, and Shu (2009); Perez-Gonzalez, Urtiaga, Ibanez, and Ortiz (2012); Rodríguez-DeLaNuez, Franquiz-Suárez, Santiago, Veza, and Sadhwani (2012); and Tong and Elimelech (2016). Some treatment options for reverse osmosis concentrates from municipal wastewater treatment have been examined by Joo and Tansel (2015); Perez-Gonzalez et al. (2012); Subramani and Jacangelo (2014). Emerging membrane technologies for water and wastewater treatment, which could also be potentially applicable for membrane concentrates, have also been discussed by Hankins, Singh, and Shen (2016). Treatment of reverse osmosis concentrates from municipal wastewater treatment (main scope being in advanced oxidation and micropollutant removal) have been also discussed in the review by Umar, Roddick, and Fan (2015). This review focuses on searching for potential solutions for efficient treatment of both nanofiltration and reverse osmosis concentrates from municipal wastewater, which can also enable the recovery of valuable components from the concentrates and thus convert concentrates from waste to value. To the best of our knowledge this is the first review article focusing entirely on the treatment of both NF and RO concentrates from municipal wastewater treatment and moreover the first review providing

comprehensive information about potential technologies for a value component recovery from these membrane concentrates. The aim is to identify also efficient membrane concentrate treatment options that could help to achieve near-zero waste process in municipal wastewater treatment. Potentially several concentrate treatment technologies are needed to be utilized together to achieve these goals set for the concentrate treatment.

2. Methods

A systematic approach was used in this literature investigation to explore all related scientific literature by using keywords in several combinations. Primary keywords were membrane concentrate, concentrate treatment, advanced wastewater treatment, municipal wastewater, and nutrient recovery. Four main databases were utilized for the literature search: Elsevier (ScienceDirect®), Emerald (Emerald Journals), EBSCO (Academic Search Elite and Business Source Complete) and SpringerLink (eJournals). From the literature search results, around 650 articles were chosen for further investigation based on the article title and abstract. Finally, 227 references focusing on topics such as membrane concentrates, advanced oxidation and nutrient recovery were included in the actual analysis, which is based on the full texts of the examined articles. The reference lists of the examined articles were also searched to allow relevant articles that were not indexed in the selected databases to be incorporated into the review. Of the 225 references utilized in this review, 51 articles (23%) were focused mainly on membrane concentrates and their treatment and 39% from these 51 articles had been published within 5 last years (Figure 1).

3. Characterization of membrane concentrates

Membrane concentrates from municipal wastewater treatment contain mainly nutrients, organic substances and various salts. Moreover, they frequently have limited biodegradability (Table 1). The specific composition of the membrane concentrate depends on the properties of the raw wastewater as well as the applied wastewater treatment process and tertiary membrane technology. In water reclamation plants, reverse osmosis or nanofiltration are often used as the final membrane filtration step to produce purified high quality water for reuse instead of discharge to the environment. In these reclamation plants, the concentrate corresponds to some extent to effluent coming from activated sludge treatment or the MBR (membrane bioreactor) process (feed for the NF or RO process), but it typically has from two to four times higher concentrations of the various
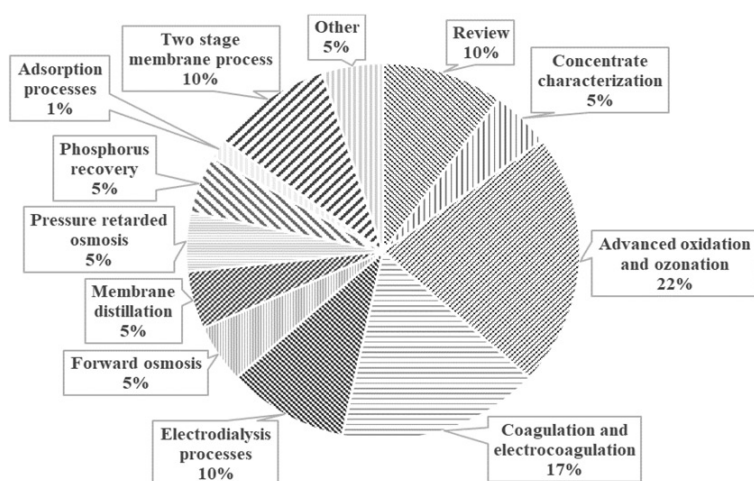
Figure 1. Classification of recent research articles related to membrane concentrate treatment.

impurities (Umar, Roddick, & Fan, 2014; Zhao, Gu, Cui, & Zhang, 2012). These concentrates are composed mainly of low molecular weight refractory organics, such as micropollutants from pharmaceuticals, pesticides and personal care products, and dissolved inorganic salts. They also contain bacteria and pathogens (Zhao et al., 2012).

In addition to various substances presented in Table 1, the membrane concentrates can also contain a wide variety of different micropollutants. Typically, the amounts of the micropollutants are really small. However, their presence might have a significant influence for the requirements of the concentrate treatment due to their potential to cause health and environmental risks. For instance, Pérez et al. (2010), Abdelmelek, Greaves, Ishida, Cooper, and Song (2011), and Benner, Salhi, Ternes, and von Gunten (2008) identified 0.1–50 µg/L concentrations of caffeine, ibuprofen, naproxen, carbamazepine and diclofenac from the RO concentrates (VRF 2–3) of municipal wastewater treatment.

The membrane concentrates from municipal wastewater treatment differ from the concentrates from desalination plants and from wastewater treatment in the mining industry in that they do not typically contain elevated concentrations of metals. However, the presence of metals depends on the wastewater sources discharging their waters to the treatment plant. Thus, it might be possible that the membrane concentrate contains also small amounts of heavy metals. Malamis et al. (2012) have shown that the RO concentrate from municipal wastewater treatment can contain around 0.1–720 µg/L of Cr, Cu, Pb and Zn, zinc being the most abundant heavy metal in the RO concentrate in their study.

Table 1. Reported characteristics of nanofiltration (NF) and reverse osmosis (RO) concentrates from municipal wastewater treatment processes (WWTP).

Parameter	Unit	NF concentrate	RO concentrate	Volume reduction factor (VRF)	References
pH	—	7.4–8.0	7.3–8.4	2.0–5.0 (NF) 2.0–6.7 (RO)	(Acero et al., 2016; Azaïs et al., 2017; Kappel et al., 2013; Miralles-Cuevas et al., 2016; Miralles-Cuevas, Oller, Agüera, Pérez, & Malato, 2017; Miralles-Cuevas, Oller, Pérez, & Malato, 2015) (NF) (Bagastyo, Radjenovic, et al., 2011; Lee, Ng, Ong, Hu, et al., 2009; Lee, Ng, Ong, Tao, et al., 2009; Pérez, Fernández-Alba, Urtiaga, & Ortiz, 2010; Umar et al., 2014; Yi Yang, Pignatello, Ma, & Mitch, 2016; Zhou, Lim, Chin, & Fane, 2011) (RO)
COD	mg/L	69–180	105–180	2.0–5.0 (NF) 4.0–6.7 (RO)	(Acero et al., 2016; Azaïs et al., 2017; Miralles-Cuevas et al., 2015, 2016) (NF) (Bagastyo, Radjenovic, et al., 2011; Umar et al., 2014; Zhou et al., 2011) (RO)
BOD$_5$	mg/L	25–43	<2	5.0 (NF) 4.0–6.7 (RO)	(Azaïs et al., 2017) (NF) (Lee, Ng, Ong, Hu, et al., 2009; Zhou et al., 2011) (RO)
[a]BDI	—	0.29–0.37	0.01–0.02	5.0 (NF) 4.0–6.7 (RO)	(Azaïs et al., 2017) (NF) (Zhou et al., 2011) (RO)
DOC	mg/L	21–60	14–61	2.0 (NF) 2.0–6.7 (RO)	(Acero et al., 2016; Azaïs et al., 2017; Miralles-Cuevas et al., 2015, 2016, 2017) (NF) (Bagastyo, Radjenovic, et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Pérez et al., 2010; Sun, Gao, Hu, Tang, & Yang, 2014; Umar et al., 2014; Yang et al., 2016; Zhou et al., 2011) (RO)
Conductivity	mS/cm	3.1–7.0	1.7–27.5	4.0–5.0 (NF) 2.0–6.7 (RO)	(Azaïs et al., 2017; Miralles-Cuevas et al., 2015, 2016, 2017) (NF) (Bagastyo, Keller, et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Pérez et al., 2010; Sun, Gao, Hu, Tang, & Yang, 2014; Umar et al., 2014; Zhou et al., 2011) (RO)
Total dissolved solids (TDS)	mg/L	—	1,100–17,400	2.5–6.7 (RO)	(Lee, Ng, Ong, Tao, et al., 2009; Sun et al., 2014; Umar et al., 2014; Zhou et al., 2011) (RO)
NO$_3^-$	mg/L	10–20	0–91	4.0 (NF) 2.0–6.7 (RO)	(Miralles-Cuevas et al., 2015) (NF) (Bagastyo, Radjenovic, et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Pérez et al., 2010; Zhou et al., 2011)(RO)
Potential value components					
PO$_4^{3-}$	mg/L	0–62	0–46	3.0–4.0 (NF) 3.0–10.0 (RO)	(Bradford-Hartke, Lant, & Leslie, 2012; Kappel et al., 2013; Miralles-Cuevas et al., 2015) (NF) (Bradford-Hartke et al., 2012; Joss et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Yang et al., 2016; Zhou et al., 2011) (RO)
NH$_4^+$	mg/L	70–150	13–301	4.0 (NF) 1.7–3.3 (RO)	(Miralles-Cuevas et al., 2015, 2016) (NF) (Malamis, Katsou, Takopoulos, Demetriou, & Loizidou, 2012; Pérez et al., 2010; Yang et al., 2016) (RO)
K$^+$	mg/L	8–180	13–75	3.0–4.0 (NF) 1.7–10 (RO)	(Bradford-Hartke et al., 2012; Kappel et al., 2013; Miralles-Cuevas et al., 2015, 2016) (NF) (Bradford-Hartke et al., 2012; Joss et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Malamis et al., 2012; Zhou et al., 2011) (RO)

Table 1. Continued.

Parameter	Unit	NF concentrate	RO concentrate	Volume reduction factor (VRF)	References
Mg^{2+}	mg/L	18–240	7–142	3.0–4.0 (NF) 3.0–10.0 (RO)	(Bradford-Hartke et al., 2012; Kappel et al., 2013; Miralles-Cuevas et al., 2015, 2016) (NF) (Joss et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Zhou et al., 2011) (RO)
Ca^{2+}	mg/L	73–280	57–546	3.0–4.0 (NF) 3.0–10.0 (RO)	Bradford-Hartke et al., 2012; Kappel et al., 2013; Miralles-Cuevas et al., 2015, 2016) (NF) (Joss et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Zhou et al., 2011) (RO)
Na^+	mg/L	84–800	92–753	3.0–4.0 (NF) 1.7–10 (RO)	(Kappel et al., 2013; Miralles-Cuevas et al., 2015) (NF) (Joss et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Malamis et al., 2012; Zhou et al., 2011) (RO)
Cl^-	mg/L	1,000–1,600	155–8,875	4.0 (NF) 2.0–10.0 (RO)	(Miralles-Cuevas et al., 2015, 2015, 2017) (NF) (Bagastyo, Radjenovic, et al., 2011; Joss et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Pérez et al., 2010; Umar et al., 2014; Yi Yang et al., 2016; Zhou et al., 2011) (RO)
SO_4^{2-}	mg/L	500–1,500	160–1,440	4.0 (NF) 2.0–6.7 (RO)	(Miralles-Cuevas et al., 2015, 2016, 2017) (NF) (Bagastyo, Radjenovic, et al., 2011; Lee, Ng, Ong, Tao, et al., 2009; Pérez et al., 2010; Yi Yang et al., 2016; Zhou et al., 2011) (RO)

[a]Biodegradability index (BDI = BOD$_5$/COD ratio) describes the biodegradability of concentrate. Substances having BDI values below 0.1 have very high resistance to biodegradation.

As can be seen from Table 1, membrane concentrates of municipal wastewater treatment are usually relatively dilute streams. The concentrates commonly have a high volume, between 15% and 50% of the initial feed volume; this corresponds to volume reduction factor values (VRF) of 2–7 (Bagastyo, Radjenovic, et al., 2011; Dialynas, Mantzavinos, & Diamadopoulos, 2008). For instance, in a wastewater treatment plant having a population equivalent of 100,000 persons, this means that a membrane concentrate volume between 3750 and 12,500 m^3/d requires treatment, assuming wastewater production of 250 L/d per person (Bradford-Hartke et al., 2012). Thus, further treatment of the membrane concentrate poses technological challenges due to its very high volume and relatively diluted nature. However, the diluted nature depends strongly on the characteristics of the wastewater treated at the plant. For instance, RO membrane concentrates with rather high total dissolved solid content (TDS 17,400 mg/L) and chloride content (8875 mg/L) and moderate concentrations of organic substances (COD 155 mg/L) was obtained, when relatively saline municipal wastewater was treated in intermittently decanted extended aeration bioreactors followed by ultrafiltration and RO (Umar et al., 2014).

4. Treatment technologies for membrane concentrate

The criteria determining the most potential technology or technologies for membrane concentrate treatment arise from the planned use or discharge points of the treated concentrate stream (Acero, Benitez, Real, & Teva, 2012; Bagastyo, Radjenovic, et al., 2011; Bagastyo, Keller, Poussade, & Batstone, 2011; Dialynas et al., 2008; Ding, Jaffrin, & Luo, 2014; Jaffrin, 2008; Lee, Ng, Ong, Tao, et al., 2009; Umar et al., 2014; Wert, Gonzales, Dong, & Rosario-Ortiz, 2011; Zhang, Van der Bruggen, Pinoy, & Meesschaert, 2009) (Figure 2). The simplest option might be the recirculation of the concentrate back to an activated sludge process (Kappel et al., 2014). This, however, is possible only for a limited time or, at least the recirculation could cause challenges in many plants, especially in long term operation, due to the low biodegradability and potentially high salt content of the membrane concentrates (Table 1). Thus, there is very often the need to apply an additional treatment step/steps for the concentrates. An option with added value for the concentrate treatment could be the concentration and recovery of valuable components such as nutrients or salts from the concentrate before recirculation of residual concentrate back to an activated sludge process. One single concentrate treatment technology might not be sufficient to enable advanced membrane concentrate treatment potentially aiming for multiple goals such as minimizing the amount of waste and chemicals used, enhancing the water quality, and recovery of valuable components from concentrate. A number of different technologies, such as shear enhanced membrane filtration (NF or RO), advanced oxidation, coagulation, activated carbon adsorption, electrodialysis and capacitive deionization, could be applied in further treatment of the membrane concentrates (Acero et al., 2012; Bagastyo, Radjenovic, et al., 2011; Bagastyo, Keller, et al., 2011; Dialynas et al., 2008; Ding et al., 2014; Jaffrin, 2008; Lee, Ng, Ong, Tao, et al., 2009; Umar et al., 2014; Wert et al., 2011; Zhang et al., 2009). In the following paragraphs the use of different technologies for treatment of the membrane concentrate are discussed.

4.1. Membrane based technologies

Various membrane based processes such as electrodialysis, forward osmosis, membrane contactors and shear enhanced membrane filtration have been tested to treat nanofiltration or reverse osmosis concentrates from municipal wastewater treatment (Arola, Kallioinen, Reinikainen, Hatakka, & Mänttäri, 2017; Arola, Kallioinen, & Mänttäri, 2014; Jamil, Loganathan, Kazner, & Vigneswaran, 2015; Naidu, Jeong, Choi, & Vigneswaran, 2017; Zhang et al., 2009). The aim in these concentrate treatment processes has been in the concentration and recovery of nutrients or salts, minimization
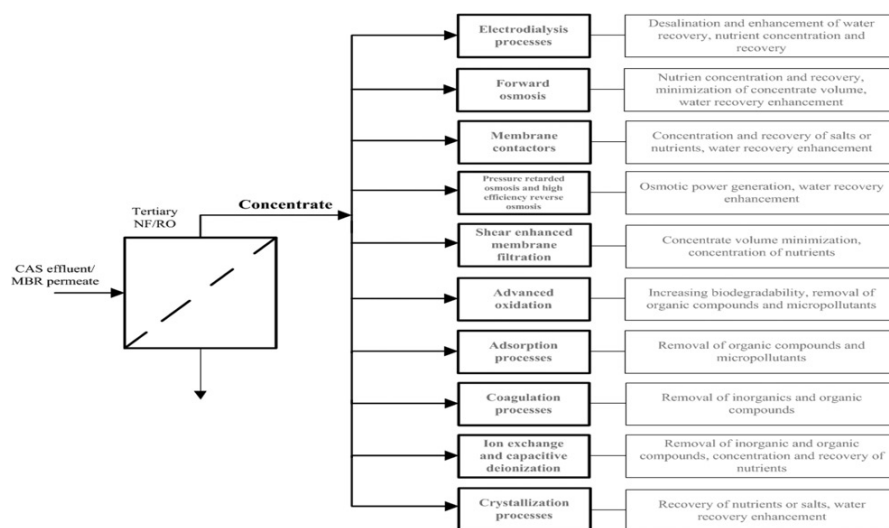
Figure 2. Technologies for advanced membrane concentrate treatment. If necessary, shear enhanced nanofiltration or reverse osmosis (NF/RO) could also be used before further concentrate treatment step such as crystallization to concentrate the membrane concentrates and potentially fractionate substances.

of concentrate volume, concentration of organics or enhancement of water recoveries.

4.1.1. Electrodialysis processes

Electrodialysis (ED) is an emerging electrochemical membrane technology in which an alternating series of cation exchange membranes (CEMs) and anion exchange membranes (AEMs), placed between the terminal anode and cathode, are used to transport ions for instance to desalinate water (Strathmann, 2010). Traditionally the major applications of ED has been in brackish water desalination, table salt production, industrial process water demineralization as well as wastewater treatment (Strathmann, 2010). According to Mehta, Khunjar, Nguyen, Tait, and Batstone (2015) electrodialysis can also be a potential method to recover nutrients, especially ammonium and potassium, from an anaerobic digester supernatant, which has passed through a centrifuge. The driving force for the ion migration through the ED membranes is a potential gradient, which is generated by applying current to the terminal electrodes (Thompson Brewster, Ward, Mehta, Radjenovic, & Batstone, 2017).

Tran et al. (2014, 2015) used electrodialysis (pH 8–12, current density 31.3–62.5 Am^{-2}, maximum voltage 12 V, 3 cell pairs) to concentrate and recover nutrients from synthetic municipal wastewaters. The phosphate concentration in the synthetic wastewater can be doubled by applying ED

treatment (pH 12, current density 62.5 Am^{-2}, maximum voltage 12 V, 3 cell pairs) using the PC-SK cation exchange membranes, the PC-SA anion exchange membranes and the PC-MVA monovalent selective anion exchange membranes (Tran et al., 2015). After concentration of phosphate with electrodialysis, the phosphorus was recovered as calcium phosphate with a high recovery rate of 83% by using crystallization (pH 11, inlet phosphate concentration 2.5 mM, Ca/P ratio 1.5, superficial velocity 61 m/h) in a pellet reactor (Tran et al., 2014).

Simultaneous recovery of ammonium and phosphorus from synthetic wastewater, which simulate sidestreams of anaerobic digestion, by coupling ED with struvite reactor have been studied by Wang et al. (2015). The wastewater that they used contained 200 mg P/L (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^{-}$) and 600 mg N/L (NH_4^{+}-N). Laboratory scale ED with the JCM-II-07 cation exchange membranes and the JAM-II-07 anion exchange membranes (membrane area 80 cm^2/membrane, current 0.6–2.0 A, current density 75–250 Am^{-2}, constant voltage 62 V,) was used to concentrate the ammonium (10–13 times concentration from 40–50 mmol/L to 400–600 mmol/L) and phosphates (10–12 times concentration from 7 to 70–80 mmol/L) before struvite crystallization (pH 9, $MgCl_2$ dose 0.5 or 1.0 mol/L). An integrated process of electrodialysis and struvite crystallization obtained removal rate of 96–100% for ammonia salt and 86–94% for phosphate.

Electrodialysis with selective ion-exchange membranes or bipolar membrane electrodialysis can also be a promising solution for membrane concentrate treatment, when the concentrate has a high conductivity (Badruzzaman, Oppenheimer, Adham, & Kumar, 2009; Yang, Gao, Fan, Fu, & Gao, 2014; Zhang et al., 2009). Zhang et al. (2009) have utilized electrodialysis for the separation of nutrient ions and organic compounds from a synthetic reverse osmosis (RO) concentrate ($MgSO_4$ 4.5 mmol/L, NaCl 7.6 mmol/L, $NaHCO_3$ 8.2 mmol/L, $NaNO_3$ 0.3 mmol/L, Na_2HPO_4 0.4 mmol/L, TOC 0 or 120 g/L) An ED cell with five cell pairs repeating PCA SK standard cation exchange membranes and PCA standard (SA) or monovalent selective (MVA) anion exchange membranes with a total membrane area of 704 cm^2 were used (Zhang et al., 2009). High removal rates of 92% for NO_3^{-} and 86% for the phosphate ions ($H_2PO_4^{-}$ and HPO_4^{2-}) was obtained with laboratory scale electrodialysis (200 min operation, 0.1–0.5 A current, current density 15.6–78.1 Am^{-2}, maximum voltage 10 V, five cell pairs) by using standard anion exchange membranes. The separation of monovalent ions such as NO_3^{-} could be further increased to 98% by using a monovalent selective membrane.

Zhang, Ghyselbrecht, Meesschaert, Pinoy, and Van der Bruggen (2011) utilized electrodialysis with the PC-SK cation exchange and PC-SA anion

exchange membranes (0.1 m^2 per membrane, total area 5.1 m^2, current 3–5 A, current density 30–50 Am^{-2}) to treat real reverse osmosis concentrate from a municipal wastewater treatment plant. The aim was to enable an increased water recovery rate in the RO process by recirculating the ED treated concentrate back to biological treatment. The conductivity of the RO concentrate decreased by 75% (from 3.5 to 0.8 mS/cm) due to the ED treatment (feed-and bleed operation, flow rate 75 L/h, applied current 3 A), which corresponded to average salt removal of 75% (75–90% removal of K$^+$, Mg^{2+}, Ca^{2+}). Post ozonation (120–576 mg/L of O$_3$) was conducted to the ED treated concentrate to enhance the biodegradability of the concentrate and reduce the accumulation of organic compounds in the circulation system. With combined ED and ozonation treatment the water recovery of RO process could be increased from 75% to 95%. Tran et al. (2012) utilized laboratory scale electrodialysis for the treatment of synthetic RO concentrate to enable the enhancement of water recovery rate of RO process by desalinating the concentrate and returning it back to the filtration process. Crystallization in a pellet reactor was utilized prior to electrodialysis with PC-SK cation exchange and PC-SA anion exchange membranes (total membrane area 0.07 m^2, current 0.45 A, current density 77.6 Am^{-2}, maximum voltage 12 V, 6 cell pairs) to remove excess calcium from the RO concentrate and prevent scaling of ED membranes. 80% calcium removal was obtained in the crystallization and this enabled stable ED treatment (60% desalination) without excessive scaling. Desalinated concentrate had a similar composition as UF influent for the RO process and could be returned back to RO process. Thus, the filtration could be carried out further, which increased overall water recovery rate. A combined treatment of crystallization and electrodialysis was seen as promising approach to enhance the water recovery of RO processes in wastewater treatment applications (Tran et al., 2012).

It can be concluded that although most studies were conducted with synthetic wastewaters, the traditional electrodialysis could be a promising technology for membrane concentrate treatment for instance as a nutrient concentration technology, especially when concentrate to be treated has a sufficient conductivity (several mS/cm). However, special attention has to be paid to membrane fouling control and potential pretreatment of wastewater when operating ED with real wastewater effluents to minimize fouling of ED membranes. Emerging applications of electrodialysis such as electrodialysis reversal (EDR) and electrodialysis metathesis (EDM) have also been examined as potential technologies for wastewater treatment (Bisselink et al., 2016; Goodman, Taylor, Xie, Gozukara, & Clements, 2013; Jaroszek, Lis, & Dydo, 2016; Yen, You, & Chang, 2017; Yin Yip & Elimelech, 2014; Zhang et al., 2017). The working principle of EDR is similar to traditional electrodialysis;

however, in the EDR the polarity of the electrodes is inverted periodically (15–30 min) to control scaling of ionic species such as calcium phosphate or carbonate (Goodman et al., 2013). Goodman et al. (2013) and Bisselink et al. (2016) have studied the utilization of EDR for the desalination of wastewater such as municipal wastewater to provide recycled water for irrigation purposes. Goodman et al. (2013) were able to reduce the total dissolved solids (TDS) of the municipal wastewater effluent from 1104 mg/L to 328 mg/L with the EDR technology, which was below the upper limit of 375 mg/L in the water quality guidelines for horticulture. The conductivity could also be decreased by 72% including the removal of calcium (84%), chloride (76%) and phosphate (60%).

Yen et al. (2017) have compared the use of EDR and RO as a last treatment steps in the wastewater reclamation process (4000 m^3/day). According to Yen et al. (2017) the RO process can provide a higher desalination rate (>97%) and lower permeate conductivity compared to the EDR process (273 μS/cm compared to 596 μS/cm). Moreover, the treatment cost is lower when applying RO (0.96 \$/m^3) as final treatment step instead of EDR (1.18 \$/m^3).

Electrodialysis metathesis (EDM) is a similar process to normal electrodialysis, however in electrodialysis metathesis the ED stack is composed of four adjacent compartments (two product compartments and two concentrate compartments) which are repeating and build up the electrodialysis metathesis stack. As a result, in the EDM process, two different salts are formed and concentrated in the two separate product compartments (Jaroszek et al., 2016). Zhang et al. (2017) have utilized EDM in an integrated system of NF-EDM to enhance the water recovery by treating NF permeate (monovalent stream) and concentrate (divalent stream) in EDM and synthesizing high solubility salts $CaCl_2$ and Na_2SO_4 into two separate product streams. A water recovery up to 98.5% was reached by an integrated process of nanofiltration and EDM. A cost comparison with RO revealed that the energy consumption of the NF-EDM process was higher compared to RO. However, the NF-EDM process could provide an even higher water recovery and lower chemical consumption. Zhang et al. (2017) Thus, EDM might be a promising technology for the treatment of NF or RO concentrate from municipal wastewater treatment in the future, but since it is still a relatively immature technology with high energy consumption and only limited data about it are available, it cannot be recommended as potential technology for concentrate treatment at this moment.

4.1.2. Forward osmosis

Forward osmosis (FO) is an emerging membrane technology which has been examined as a potential technology for municipal wastewater

treatment as well as membrane concentrate treatment to concentrate and recover nutrients (Ansari, Hai, Price, Drewes, & Nghiem, 2017; Ansari, Hai, Price, & Nghiem, 2016; Holloway, Childress, Dennett, & Cath, 2007; Qiu, Law, Das, & Ting, 2015; Qiu, Zhang, Srinivasa Raghavan, Das, & Ting, 2016a, 2016b; Xue, Tobino, Nakajima, & Yamamoto, 2015; Xue, Yamamoto, & Tobino, 2016), minimize membrane concentrate volume (Jamil et al., 2015), concentrate organics (Hey et al., 2017; Zhang, Ning, Wang, & Diniz da Costa, 2014) and enhance the total water recoveries in desalination and water reclamation plants (Jamil et al., 2015; Martinetti, Childress, & Cath, 2009). Forward osmosis is an osmotically driven membrane process where a feed solution is concentrated and its volume is minimized due to diffusion of water through semipermeable membrane from the feed solution having a lower osmotic pressure to a solution of higher solute concentration and thus higher osmotic pressure (called the draw solution, DS) (Holloway et al., 2007; Martinetti et al., 2009). As water diffuses through the membrane, the draw solution is diluted and the feed solution is concentrated, thus the draw solution must be recovered with processes such as nanofiltration, reverse osmosis, membrane distillation or electrodialysis or then replaced to maintain the driving force and keep the FO process continuously running (Ansari et al., 2017; Holloway et al., 2007; Martinetti et al., 2009). A schematic illustration of FO process utilizing either pressure driven membrane filtration (NF or RO), thermally driven membrane distillation or electrically driven electrodialysis for draw solution recovery is presented in Figure 3 (Ansari et al., 2017).

Jamil et al. (2015) utilized a forward osmosis cell (20 mm width, 3 mm height and 210 mm length) with a cellulose triacetate membrane (0.74 nm pore size) and 2–3 M NaCl as a draw solution to minimize the volume of RO concentrate from the water reclamation RO plant operating at 80% recovery rate. The use of five repeated FO steps (average fluxes 12.6, 9.7, 9.1, 13.5 and 12.7 L/m^{2}h in five FO steps) allowed to reduce the volume of RO concentrate from 20% to 8%. Flux decline of 34.0, 49.5, 52.6, 29.7 and 43.3% was observed in five FO steps, but it could be efficiently controlled by reducing the feed solution pH from 7.5 to 5.0 (last two steps at pH 5.0). The removal of micropollutants with FO was also studied; however, only a limited removal of micropollutants such as caffeine (44%), carbamazepine (52%) and diclofenac (52%) was achieved with FO (Jamil et al., 2015). Martinetti et al. (2009) also studied FO as a technology to enrich RO concentrate and thus to increase the water recovery in the desalination of brackish water. RO concentrates having high total dissolved solids content of 7500 and 17,500 mg/L were desalinated with a forward osmosis bench-scale membrane test unit containing flat sheet cellulose triacetate membranes and 50 g/L NaCl as a draw solution. The draw solution was
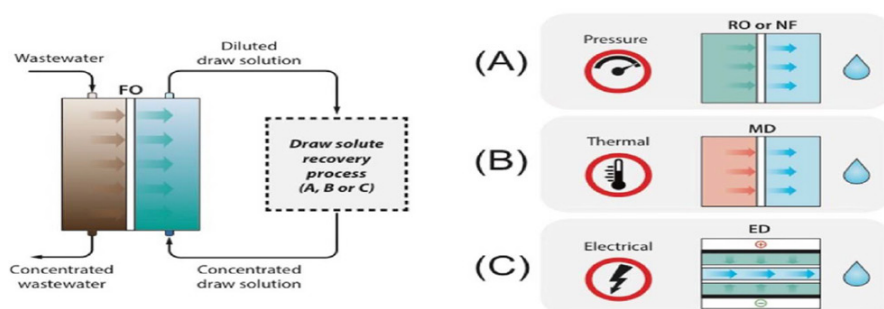
Figure 3. Schematic illustration of the forward osmosis process (FO) combined with pressure driven (A), thermally driven (B) or electrically driven (C) draw solution recovery (Ansari et al., 2017).

regenerated and kept at constant concentration by using pilot scale reverse osmosis system. The total water recoveries could be increased to above 95% with FO treatment of RO concentrates (60–70% recovery rates observed in RO desalination). Scale formation (precipitation of inorganic salts) on the FO membrane surface was observed during the FO treatment. However, scaling could be removed almost entirely by cleaning via osmotic back-washing, where the draw solution was replaced by deionized water and feed solution with a draw solution (100 g/L NaCl) and thereby reversing the flow for 20 minutes.

Seawater and seawater brine from RO desalination have been used in several studies as a draw solution to FO processes, which have been aiming to concentrate and recover nutrients, especially phosphorus from municipal wastewater (Qiu et al., 2015; Xue et al., 2015, 2016). Qiu et al. (2015) used a hybrid microfiltration-forward osmosis membrane bioreactor to recover phosphorus directly from anaerobic municipal wastewater. Cellulose triacetate FO membranes (0.072 m^2, flux 4.1–5.2 L/m^{2}h) submerged in the bioreactor were used to concentrate nutrients (PO$_4^{3-}$-P, NH$_4^+$-N) and a microfiltration membrane (PVDF, $\leq$0.1 μm pore size, 0.009 m^2, flux 4.6–9.3 L/m^{2}h) submerged in the same bioreactor was used to separate the concentrated nutrient solution and water from the sludge. Phosphorus was then recovered as calcium phosphate from the microfiltration (MF) permeate in a separate reactor (NaOH dosing to increase pH to 8.5–9.5, constant stirring 100 rpm). 90% removal of total organic carbon and 99% removal of NH$_4^+$-N could be achieved in the FO process. 97.9% of the phosphate phosphorus could be rejected and concentrated up to 7-fold by FO process using seawater RO concentrate (58 g/L of dissolved salts) as a draw solution. Over 90% overall phosphorus recovery was achieved with the combined process of microfiltration, forward osmosis and phosphorus precipitation at pH 9.0. Hybrid process combining FO and MF in a

bioreactor can recover phosphorus efficiently from municipal wastewater. However, the salt accumulation within the bioreactor can remain as a major challenge (Qiu et al., 2015). Xue et al. (2016) also utilized seawater-driven forward osmosis to concentrate nutrients from the MBR permeate of anaerobic municipal wastewater treatment. Commercial flat sheet cellulose triacetate FO membrane was used in a cross flow membrane unit (167 mm length, 36 mm width, 1.4 mm height) to concentrate nutrients from MBR permeate (pH 7.9, conductivity 1.6 mS/cm, pre-disinfected with 20 mg/L free Cl^- after 18 days of operation) by using synthetic seawater as a draw solution (35 g/L dissolved salts, conductivity 42.8 mS/cm). 3- to 4-fold concentration for total phosphorus and 2.1-fold concentration for ammonia was reached with this laboratory scale FO process. Only 5% flux decline (from initial 4.63 L/m²h to 4.40 L/m²h) was observed during 2 month operation of FO process without any fouling control conducted.

As described above, forward osmosis has been studied relatively widely as a technology to treat municipal wastewaters and especially concentrate and recover nutrients. The FO technology is currently mainly done on laboratory scale and there are still some major technical challenges such as contaminant accumulation in the draw solution, salinity accumulation as well as membrane fouling (Ansari et al., 2017). One other very important aspect concerning the feasibility of FO is the draw solution recovery. In order to be viable process the draw solution should be recovered in most cases for instance with reverse osmosis, nanofiltration, distillation, membrane distillation or electrodialysis (ED) (Ansari et al., 2017; Martinetti et al., 2009; Van der Bruggen & Luis, 2015; Xie, Shon, Gray, & Elimelech, 2016). Possible draw solutions for FO and their recovery have been studied extensively in several reviews (Ansari et al., 2017; Johnson, Suwaileh, Mohammed, & Hilal, 2018; Lutchmiah, Verliefde, Roest, Rietveld, & Cornelissen, 2014; Qingchun, Mingming, & Tai-Shug, 2013; Shaffer, Werber, Jaramillo, Lin, & Elimelech, 2015; Valladares Linares et al., 2014; Van der Bruggen & Luis, 2015; Wang, Goh, Li, Setiawan, & Wang, 2018; Xie et al., 2016; Zhao, Zou, Tang, & Mulcahy, 2012). According to Ansari et al. (2017) some post-treatment methods may be necessary if ED is used for draw solution recovery, since it has relatively low removal capacity for organic compounds. When considering the other common draw solution recovery techniques the reverse osmosis is in many cases the most commonly used option as it allows production of more concentrated draw solutions than nanofiltration and it is energetically favorable over distillation (unless waste heat is readily available) (Ansari et al., 2017; Shaffer et al., 2015; Wang et al., 2018). In order to be an efficient treatment process the FO needs rather strong draw solution to enable sufficient driving force. Thus, at the moment FO process can be considered as potential membrane

concentrate treatment technology only in the areas where a concentrated draw solution is readily and cost efficiently available and can be recovered as a part of integrated solution (Van der Bruggen & Luis, 2015).

4.1.3. Membrane contactors

Membrane contactor processes, such as membrane crystallization (Chabanon, Mangin, & Charcosset, 2016; Edwie & Chung, 2012; Li, Van der Bruggen, & Luis, 2014, 2016; Macedonio et al., 2011), membrane distillation (Edwie & Chung, 2012; Husnain, Liu, Riffat, & Mi, 2015; Kim et al., 2015; Martinetti et al., 2009; Naidu et al., 2017; Xie et al., 2016) and liquid-liquid membrane contactors (Darestani, Haigh, Couperthwaite, Millar, & Nghiem, 2017; Licon Bernal, Maya, Valderrama, & Cortina, 2016; Sancho et al., 2017; Wäeger-Baumann & Fuchs, 2012) have been studied as a potential technologies for wastewater and membrane concentrate treatment to concentrate and recover salts or nutrients or to enhance the water recovery rates.

Membrane crystallization can be conducted as either hybrid membrane crystallization or integrated membrane crystallization (Chabanon et al., 2016). In the hybrid crystallization, the membrane module is used to create supersaturation of precipitating substances and concentration of the solid phase, but the actual nucleation and crystal formation and growth takes place in a separate crystallizer (Chabanon et al., 2016). In the integrated membrane crystallization both the supersaturation as well as the crystal formation and growth is occurring inside the membrane module (Chabanon et al., 2016). Membrane crystallization can be utilized to recover salts (see section 5.2) such as sodium sulfate and sodium carbonate from aqueous solutions or to increase the water recovery rates of RO desalination plant (Li et al., 2014, 2016; Macedonio et al., 2011). Li et al. (2016) utilized two stage membrane crystallization for the recovery of Na_2CO_3 and Na_2SO_4 from mixed aqueous solution of these sodium salts (160–200 g/L Na_2CO_3 and 60 g/L Na_2SO_4). Liquid-Cel polypropylene hollow fiber membrane (0.04 μm pore size, 0.18 m^2 membrane area) was used to crystallize Na_2CO_3 in the first stage and concentrate Na_2SO_4 by using NaCl (300 g/L) as the osmotic solution and then after $CaCO_3$ precipitation the Na_2SO_4 was crystallized in the second crystallization stage by using the same osmotic solution. Up to 40.5% recovery rate for Na_2CO_3 and 54% for the Na_2SO_4 was reached with the membrane crystallization. Quist-Jensen, Macedonio, Horbez, and Drioli (2017) utilized membrane crystallization for the recovery of Na_2SO_4 from industrial wastewater containing 45–55 g/L of Na_2SO_4 and concluded that above 75% recovery rates for sodium sulfate can be obtained by membrane crystallization treatment while maintaining stable trans-membrane flux. Research related to membrane crystallization has been done mainly on laboratory scale and the technology appears to be

more suitable for industrial wastewater streams having a very high salt content rather than for the membrane concentrates from municipal wastewater treatment (Li et al., 2014, 2016; Quist-Jensen et al., 2017). Thus, membrane crystallization is not considered as a treatment technology with high potential for NF or RO concentrates from municipal wastewater treatment.

Membrane distillation (MD) is a thermally driven membrane separation process, where two aqueous solutions are separated from each other by a porous hydrophobic membrane due to partial vapor pressure (Kim et al., 2015; Naidu et al., 2017; Xie et al., 2016). In MD the water is moving across the membrane as water vapor from the feed side (hot saline water) to the distillate (permeate) side and thus complete retention of nonvolatile substances can be achieved (Kim et al., 2015; Xie et al., 2016).

Martinetti et al. (2009) utilized vacuum enhanced direct contact membrane distillation (VEDCMD) to enrich RO concentrate and thus to increase the overall water recovery in the desalination of brackish water. RO concentrates having a high total dissolved solids content of 7500 (concentrate A) and 17,500 mg/L (concentrate B) were treated with a bench-scale membrane test unit containing flat sheet polytetrafluoroethylene (PTFE) or polypropylene (PP) membranes with a pore size of 0.22 μm, membrane surface area of 0.0139 m^2 and water fluxes between 5 and 40 L/m^2h (experiments stopped when flux declined to 5 L/m^2h). RO concentrate was added to the feed reservoir and heated to 40 or 60 °C, whereas deionized water cooled to 20 °C was used as initial permeate. The total water recoveries could be increased to above 89% (concentrate A) and 98% (concentrate B) with MD treatment of RO concentrates (60–70% recovery rates observed in RO desalination) (Martinetti et al., 2009). Naidu et al. (2017) utilized direct contact membrane distillation for RO concentrate treatment. Membrane distillation (MD) was used to increase the overall recovery rate of RO process and concentrate ions such as PO_4^{3-}, Ca^{2+} and Mg^{2+} to enable their precipitation in the further concentrate treatment. Direct contact membrane distillation using hydrophobic PTFE flat sheet membrane with 0.004 m^2 membrane area and 0.2 μm was used to treat RO concentrate heated to a 55 °C (pH 8.0, TDS 1.49 g/L, turbidity 0.11 NTU, DOC 58–60 mg/L, Na^+ 445 mg/L, Cl^- 605 mg/L, $CaCO_3$ hardness 459 mg/L). Deionized water with a temperature of 25 °C was used as initial permeate. 85% recovery of RO concentrate was achieved with membrane distillation with 13–25% flux decline (flux decline from initial 16 kg/m^2h to 12–14 kg/m^2h). In addition, 99% ion retention was obtained in MD process, and thus several inorganic ions such as Ca^{2+} and Mg^{2+} were saturated in the MD concentrate (Naidu et al., 2017). The major challenge in the MD processes is membrane fouling. MD is also an emerging technology, which requires a significant amount of thermal energy. Thus, it might not be a

widely feasible treatment technology for membrane concentrates from municipal wastewater treatment plants.

Liquid-liquid membrane contactors usually utilize hydrophobic hollow fiber membranes to transfer gaseous species, especially ammonia gas, across the membrane from the feed side to the permeate side; thus enables nutrient recovery from wastewaters (Darestani et al., 2017). Licon Bernal et al. (2016) and Sancho et al. (2017) have used hollow fiber liquid-liquid membrane contactors for the ammonia recovery from municipal wastewater effluents. Licon Bernal et al. (2016) utilized the Liquid-Cel Extra Flow X30HF polypropylene hollow fiber membrane (pore size $0.03\,\mu m$, membrane surface area $1.4\,m^2$) in a liquid-liquid membrane contactor to concentrate and recover ammonia as diammonium phosphate from ammonia concentrates ($1–3\,g$ NH_3/L in $1–2\,g$ NaOH/L). These concentrates were generated by removal of ammonium from tertiary municipal wastewater treatment effluents by zeolites. Recoveries of 93–98% for diammonium phosphate were achieved with liquid-liquid membrane contactors by using phosphoric acid in the stripping solution; the concentration of ammonia could be increased to $10–12\,g/L$. The nutrient solution produced with a liquid-liquid membrane contactor was rich in ammonium salt and had a high purity since only gaseous species can be transported through the membrane; thus, the concentrated solutions was seen as potential product to be as liquid fertilizer applications. Sancho et al. (2017) utilized a similar approach as Licon Bernal et al. (2016) to concentrate ammonia and recover it as liquid fertilizer by using a liquid-liquid hollow fiber membrane contactor. A membrane contactor was used to treat ammonium concentrates ($2–3\,g$ NH_3/L) from tertiary municipal wastewater treatment (zeolite column adsorbing ammonium from wastewater effluent). A liquid-liquid membrane contactor using the Liquid-Cel Extra Flow X30HF polypropylene hollow fiber membrane was able to reach over 98% recovery rate for ammonia and ammonium could be recovered as a concentrated diammonium phosphate solution ($20–50\,g/L$).

Liquid-liquid hollow fiber membrane contactor technology is thought a promising approach to concentrate and recover ammonium from municipal wastewater. However, it would be beneficial to have a relatively concentrated feed solution for the membrane contactor process ($\geq 1\,g$ NH_3/L). Thus, as a single treatment technology, liquid-liquid membrane contactor is not considered a high-potential membrane concentrate treatment option in municipal wastewater treatment where the ammonium concentrations in the concentrates are usually below $1\,g/L$ (Table 1).

4.1.4. Pressure retarded osmosis and high efficiency reverse osmosis

Pressure retarded osmosis (PRO) has been studied as a potential membrane concentrate treatment technology to generate osmotic power from salinity

gradients between a membrane concentrate and a draw solution, and to enhance the water recoveries in RO desalination plants (Altaee, Millar, & Zaragoza, 2016; Chung, Banchik, Swaminathan, & Lienhard V, 2017; Kim, Kim, Shon, & Hong, 2015; Wan & Chung, 2015; Yin Yip & Elimelech, 2014). High efficiency reverse osmosis (HERO) is used in water desalination to increase the water recovery rates (Chen, Baygents, & Farrell, 2017). PRO is an osmotically driven membrane process, which generates renewable energy by utilizing the osmotic gradient between two streams, having a different salinity (Altaee et al., 2016; Kim et al., 2015). In PRO water permeates through the osmosis membrane from water with lower salinity such as RO concentrate from water reclamation plant into a draw solution having a high salinity such as seawater RO brine (Kim et al., 2015).

Wan and Chung (2015) utilized PRO using seawater brine as the draw solution and membrane concentrate from the NEWater plant (plant producing drinking water from municipal wastewater) as the feed solution to generate osmotic power. A thin film composite polyethersulfone hollow fiber membrane ($3.5 \, L/m^2h$ bar permeability) prepared by the researchers was used in the PRO process. Water fluxes of $8–10 \, L/m^2h$ and $4.55 \, W/m^2$ power density were obtained in PRO when membrane concentrate (osmolality 22 mmol, pH 7.44, TOC 44 mg/L) was used as the feed solution and seawater brine (osmolality 1468 mmol, pH 7.3, TOC 66 mg/L) as the draw solution. The obtained power density was relatively modest and membrane fouling was a problem. Thus, membrane concentrate was prefiltered with nanofiltration (polyamide NE2540-70 membrane, molecular weight cutoff, 200 Da) before the PRO process. After the NF pretreatment, which reduced the fouling tendency by removing almost 50% of the TOC, 66% of the sulfate and 43% of the calcium, the power density in the PRO could be increased to $8.9 \, W/m^2$. This power density was higher than the $5 \, W/m^2$ proposed by hydropower company Statkraft as a limit value for an economically viable process. Chung et al. (2017) have made an economic viability analysis for pressure retarded osmosis as a stand-alone process. Based on their research the PRO process has potential and is economically viable only then, when a draw solution having extremely high salinity (above 18%) can be used. Thus, the PRO process is considered as a potential membrane concentrate treatment technology only in very limited areas where high salinity water such as RO concentrate from seawater desalination plant can be utilized as a draw solution.

Ion exchange resins could be utilized for membrane concentrates to remove excessive scaling components such as calcium (reducing water hardness) from the concentrate. An example of this kind of process is HERO process, which utilizes weak acid cation exchange media as a first step to remove Ca^{2+}, and Mg^{2+} from the feed water and then the feed

water is decarbonized by removing dissolved CO_2. After these steps, the pH of the feed water is increased to ≥ 9 to reduce the fouling of the RO membrane (Chen et al., 2017). As high as 99% permeate recoveries can be achieved in RO desalination processes by applying the HERO process, according to Chen et al. (2017). HERO processes are especially designed for the treatment of waters with high silica concentration (≥ 1500 mg/L) and thus the process usually produces a concentrate rich in silica compounds. The treatment of this HERO concentrate rich in silica can be challenging and only limited research data are available about the HERO process related to its application for municipal wastewater treatment (Chen et al., 2017).

4.1.5. Shear enhanced membrane filtration

Several shear enhanced membrane module types with wider flow channels than spiral-wound modules have been developed (Figure 4) for use with challenging and concentrated effluents like membrane concentrates. A high shear rate can be created on the membrane surface by using moving parts such as a rotating disc, rotor or rotating membrane, or by vibrating the membrane (Figure 4, Table 2) (Ding et al., 2014; Jaffrin, 2008; Postlethwaite, Lamping, Leach, Hurwitz, & Lye, 2004; Subramani, DeCarolis, Pearce, & Jacangelo, 2012). The high turbulence created at the membrane surface in shear enhanced membrane filtration hinders the formation of a concentration polarization layer and increases the permeate flux. In addition, membrane fouling can potentially be decreased, the membrane selectivity improved, and the formation of unwanted precipitates on the membrane prevented. As in these shear enhanced membrane modules the flow conditions are significantly enhanced to a more turbulent flow it will enable the concentration of the feed solution to a higher volume reduction factor values compared to the traditional spiral wound modules. This opens new possibilities for a value component recovery from membrane concentrate. For instance, Arola et al. (2014), and Arola, Kallioinen, et al. (2017) reported overall recovery rates up to 99.7% (VRF 300) in the treatment of membrane concentrate from municipal wastewater treatment with vibratory shear enhanced processing technology (VSEP filter) and a cross rotational CR filter. Obviously, the smaller the amount of concentrate, the smaller the devices in the final treatment of the concentrate. The low volume of concentrate also enables the use of different treatment and nutrients recovery methods, which are not so feasible with large volumes. The low volume is typically linked with a high concentration of solute compounds e.g., phosphorous, which facilitates its recovery by crystallization.
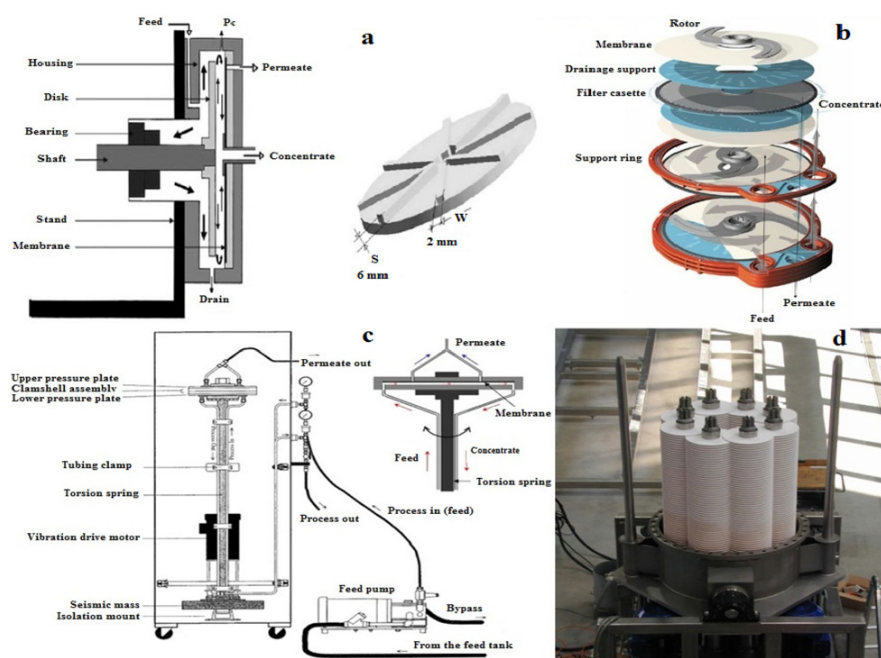
Figure 4. Schematic structure of shear enhanced membrane processes. Rotating disk module with vanes (a), cross rotational OptiFilter CR-1010 with a rotating rotor (b), vibratory shear enhanced processing technology (VSEP) series L (c) and an industrial MSD (multishaft disk system) module with eight parallel shafts and 31 cm rotating ceramic membrane disks (d) (Frappart, Akoum, Ding, & Jaffrin, 2006; Jaffrin, 2008; Luo et al., 2012; Nurminen, 2011; Petala & Zouboulis, 2006).

There is a number of examples of the use of shear enhanced membrane filtration in demanding applications such as filtration of landfill leachates and pulp and paper industry process waters and liquors (Table 2). VSEP technology has been utilized in landfill leachate filtration (Chan et al., 2007; Zouboulis & Petala, 2008) and brackish water reverse osmosis concentrate treatment (Subramani et al., 2012), whereas cross rotational (CR) filters utilizing rotor blades have been widely used in the treatment of pulp industry effluents (Kallioinen et al., 2010; Mänttäri, Kuosa, Kallas, & Nyström, 2008; Mänttäri, Pekuri, & Nyström, 2004; Mänttäri & Nyström, 2007; Tirkkonen, Arola, Veijonen, Mänttäri, & Kallioinen, 2015). Recently, the CR-filters have also been tested in municipal wastewater treatment (Arola, Kallioinen, et al., 2017; Mänttäri & Nyström, 2007). Several technologies with rotating discs or membranes have been studied for the treatment of various challenging effluents such as dairy wastewater, microalgae, mineral suspensions and black liquor (Bhattacharjee & Bhattacharya, 2006; Ding, Jaffrin, Mellal, & He, 2006; Engler & Wiesner, 2000; Frappart et al., 2006; Hwang & Lin, 2014). Other shear enhanced technologies that have

Table 2. Characteristics and application areas of shear enhanced membrane filtration.

Shear enhanced technology	Model	Membrane area, m²	Membrane filtration range	Pressure range, bar	Flux range, L/m²h	Shear rate, rpm	Reported application areas	Advantages and Challenges	Reference
Fixed membrane with rotating disk	Laboratory built RDM module with or without 6 mm high vanes; Laboratory built rotating disk filter with 10 mm high vanes	0.0176 0.00112	MF to RO (mainly UF and NF) MF	0–40 0.1–1	25–500 30–100	500–2500 (5×10^4–4.43×10^5 s^{-1}) 0–500	Dairy effluent treatment, Detergent wastewater treatment, Microalgae concentration	High shear rate, broad pressure range, high energy and capital cost for full scale application compared to VSEP Efficient microalgae concentration, moderate flux (30–100 L/m²h in MF)	(Frappart et al., 2006; Hwang & Lin, 2014; Luo, Cao, et al., 2012; Luo, Ding, Wan, & Jaffrin, 2012a, 2012b, Luo, Ding, Wan, Paullier, & Jaffrin, 2010, 2012)
Fixed membrane with rotors	CR200/1 CR250 CR350 CR550/10 CR1000/10 OptiFilter CR1010/ 100, Metso	0.054 0.09 1.0 3.75 13.5 140	MF to high permeability NF (mainly UF)	0–2 (CR200) 0–8 (CR250, CR350) 0–6 (1000 series)	30–450	0–1000 (rotor rotating speed, peripheral velocity 0–13 m/s)	Pulp and paper industry effluent treatment, Municipal wastewater treatment	High shear rate, high filtration capacity, can withstand small solids and fibers, limited pressure range	(Arola, Kallioinen, et al., 2017; Huuhilo, Väisänen, Nuortila-Jokinen, & Nyström, 2001; Jaffrin, 2008; Kallioinen et al., 2010; Mänttäri et al., 2008; Mänttäri & Nyström, 2007; Mänttäri et al., 2004; Tirkkonen et al., 2015)
Rotating membranes	MSD (multishaft disk) system, Aaflowsystems Industrial scale unit, Westfalia Separator Stirred rotating disc module	0.121 (6 ceramic membrane disc pilot) 80 (industrial scale)	MF to UF	0–4 0–8	50–900 12–25	500–1500 (membrane rotational speed, 1–2×10^5 s^{-1}) 0–1000 (stirring speed), 0–600 (membrane rotation)	Filtration of mineral suspensions Ultrafiltration of black liquor	Comparably low energy consumption in industrial scale (energy costs 0.64 €/m³ of permeate), but significant energy consumption in pilot scale (4.2–11.6 kWh/m³ of permeate), limited pressure range	(Bhattacharjee & Bhattacharya, 2006; Ding et al., 2006; Jaffrin, 2008)

Table 2. Continued.

Shear enhanced technology	Model	Membrane area, m²	Membrane filtration range	Pressure range, bar	Flux range, L/m²h	Shear rate, rpm	Reported application areas	Advantages and Challenges	Reference
Vibrating membranes	VSEP L (lab scale) VSEP LP (pilot scale) VSEP (industrial scale) MMV (magnetically induced membrane vibration) system	0.0503 1.57 150 0.016 / module	MF to RO (mainly NF and RO) MF to loose UF	0–40 —	50–400 10–50	$1.4–1.5 \times 10^5$ s^{-1}, resonant frequency around 60 Hz Vibration frequency 45 Hz	Treatment of landfill leachates, brackish water RO concentrates, forest industry effluents such as UF concentrates, contaminated surface waters, biogas effluents Harvesting microalgal biomass	High shear rate, broad pressure range, comparably low energy consumption in industrial scale (<2.5 kWh/m³), possible sealing problems if very concentrated solutions are filtered Relatively energy efficient (<1 kWh/m³), limited applications areas	(Bilad et al., 2013; Chan et al., 2007; Ding et al., 2014; Huuhilo et al., 2001; Jaffrin, 2008; LINPAC, 2005; Luo, Cao, et al., 2012; Nuortila-Jokinen, Kuparinen, & Nyström, 1998; Petala & Zouboulis, 2006; Subramani et al., 2012; Zouboulis & Petala, 2008)
Vibrating hollow fiber module	Laboratory built vibrating hollow fiber MF system	0.0256 0.0488 0.0057	MF	<1	5–90	$20–2 \times 10^3$ s^{-1}, Vibration 0–30 Hz $10–3 \times 10^3$ s^{-1}, Vibration 5–25 Hz $0–3 \times 10^3$ s^{-1}, Vibration 0–10 Hz	Filtration of yeast solutions, separation of enzymes from yeast suspensions	Minimal fouling below critical flux (negligible change in fouling resistance), limited application areas	(Beier, Guerra, Garde, & Jonsson, 2006; Beier & Jonsson, 2007; Genkin et al., 2006)
Spinning basket module	Laboratory built spinning basket membrane module	0.0286	UF	2.9–5.9	—	200–500 (basket rotational speed)	Filtration of Bovine Serum Albumin (BSA)	Improved fouling control compared to the traditional rotating disk module ($\leq 10\%$ flux decline after 5 h continuous operation), limited pressure range	(Sarkar et al., 2012)

been the subject of study adopt approaches like the use of vibrating hollow fiber modules (Beier & Jonsson, 2007; Genkin, Waite, Fane, & Chang, 2006), spinning basket membrane modules (Sarkar, Moulik, Sarkar, Roy, & Bhattacharjee, 2012) and membrane modules with magnetically induced vibration due to magnetic attraction and repulsion forces (Bilad et al., 2013).

Of the shear enhanced technologies presented in Table 2, the VSEP technology, described by Luo, Cao, et al. (2012) and Petala and Zouboulis (2006), is assumed to have a great potential for the concentration of effluents and membrane concentrates from municipal wastewater treatment. This is because it creates a good turbulence on the membrane surface, is available at an industrial scale and, if necessary, can be used with high pressures. According to the literature, the use of CR filters is also possible, since CR filters can be used with nanofiltration membranes (pressure limit 6–8 bar), a high turbulence can be created with rotor blades, industrial scale modules are available, and the module can tolerate some solids (Table 2). Other shear enhanced membrane filtration technologies presented in Table 2 are mainly available only at laboratory scale. Potentially, tubular modules could also be utilized for concentrate treatment, since turbulent conditions can be created inside the module by increasing the pumping velocity; however, this strongly influences the energy consumption (Schäfer, Fane, & Waite, 2005).

4.2. Advanced oxidation technologies

The performance of advanced oxidation processes (AOPs) is based on the formation of highly reactive radicals, mainly hydroxyl radicals and ozone, *in situ* at near ambient temperature and pressure, which oxidize and partially degrade organic compounds in water (Black & Veatch Corporation, 2010; Panorel, Kornev, Hatakka, & Preis, 2011; Ribeiro, Nunes, Pereira, & Silva, 2015). The hydroxyl radical ($\cdot$OH) is a highly effective and nonselective chemical oxidant, which has a very high oxidation potential of 2.80 V compared to the 2.07 V of ozone. $\cdot$OH reacts readily with most organic substances (Black & Veatch Corporation, 2010; Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012; Ribeiro et al., 2015). The radicals can be produced in various ways; correspondingly, AOPs can be classified as ozone based, hydrogen peroxide based, photocatalysis, ultrasound, electrochemical, electron beam and non-thermal plasma oxidation (Black & Veatch Corporation, 2010; Crittenden et al., 2012; Dobrin, Bradu, Magureanu, Mandache, & Parvulescu, 2013; Mehrjouei, Müller, & Möller, 2014; Michael-Kordatou et al., 2015; Panorel, Preis, Kornev, Hatakka, & Louhi-Kultanen, 2013; Ribeiro et al., 2015). A number of advanced

oxidation processes (AOPs) have been utilized for wastewater treatment and membrane concentrate treatment (Table 3) at laboratory scale (Acero et al., 2016; Bagastyo, Radjenovic, et al., 2011; Dialynas et al., 2008; Pérez et al., 2010; Umar et al., 2014; Yang et al., 2016). Some of them, especially ozonation, have been used on a pilot and industrial scale for the removal of organic compounds such as micropollutants from municipal wastewater effluents such as membrane concentrates (Azaïs, Mendret, Cazals, Petit, & Brosillon, 2017; Benner et al., 2008; Miralles-Cuevas et al., 2016; Miralles-Cuevas et al., 2017, Miralles-Cuevas et al., 2015; Reungoat et al., 2010). In the treatment of membrane concentrates, AOPs can be used to remove organic compounds, to degrade micropollutants such as pharmaceuticals, to disinfect the concentrate, and to increase the biodegradability of the concentrate in order to enhance concentrate recyclability and ensure the safety of concentrate disposal or end use (Bagastyo, Radjenovic, et al., 2011; Dialynas et al., 2008; Pérez et al., 2010; Reungoat et al., 2010; Umar et al., 2014). Various advanced oxidation techniques have been also studied in depth in several reviews focusing directly on the advanced oxidation treatment of various wastewaters including membrane concentrates (Ganiyu, Van Hullebusch, Cretin, Esposito, & Oturan, 2015; Joo & Tansel, 2015; Kanakaraju, Glass, & Oelgemöller, 2018; Michael-Kordatou et al., 2015; Miklos et al., 2018; Oller, Malato, & Sánchez-Pérez, 2011; Tijani, Fatoba, Madzivire, & Petrik, 2014).

Although the degradation of organic substances such as micropollutants in AOPs (Table 3) is based largely on the generation of hydroxyl radicals ($\cdot$OH), ozone also plays a role. Ozone and especially hydroxyl radicals are unselective and strongly oxidizing species that attack the aromatic organic structures of organic micropollutants (Ribeiro et al., 2015). In AOP, the micropollutants split to core molecules and complete mineralization is not usually aimed (Luis, Saquib, Vinckier, & Van der Bruggen, 2011) to limit the oxidation energy. Due to the high efficiency of AOP in the degradation of pharmaceuticals from membrane concentrates (Table 3), AOP can make a major contribution to ensuring the safety of concentrate disposal (Pérez et al., 2010). In some AOP processes, factors other than ozone and hydroxyl radicals can facilitate the degradation of micropollutants, for example, hydrogen peroxide, UV light and hypochlorite. For instance, in electrochemical oxidation of moderate to high salinity RO concentrate, strong oxidants such as hypochlorite were reported to contribute to the degradation of organic pollutants (Bagastyo, Radjenovic, et al., 2011; Pérez et al., 2010).

The disadvantage of some AOPs is their relatively high energy consumption (Table 3). The presence of organic impurities other than micropollutants, mainly effluent organic matter, competes for the oxidants and thus

Table 3. Advanced oxidation processes utilized for membrane concentrates of municipal wastewater treatment.

AOP technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
Ozonation	Direct ozonation, effective dose 5–11 mg O_3/L	Removal of micropollutants mainly beta blockers from WWTP RO concentrate	90% removal of propranolol (8 mg O_3/L) and metoprolol (11 mg O_3/L)	Optimization of ozone dose and formation of unknown oxidation by-products, energy consumption not reported	(Benner et al., 2008)
	Direct ozonation, effective dose 0.35 mg O_3/mg of DOC (10 mg O_3/L)	Removal of micropollutants from WWTP NF concentrate (VRF 2)	>95% removal of diclofenac, 80–90% removal of acetaminophen and metoprolol, 45–50% removal of caffeine	Optimization of ozone dose, limited removal of pollutants recalcitrant to ozone (caffeine), energy consumption not reported	(Acero et al., 2016)
	Direct ozonation, effective dose 1.7 mg/min L (0–74 mg O_3/L)	Removal of acetaminophen, carbamazepine and atenolol from WWTP NF concentrate (VRF 5) and identification oxidation by-products	>95% removal of acetaminophen and carbamazepine, 40–50% removal of atenolol (28 mg O_3/L)	Limited removal of beta blocker atenolol at lower ozone dosages, energy consumption not reported	(Azaïs et al., 2017)
Electro-chemical oxidation	Boron doped diamond (BDD) electrode, current density 50–200 A/m², oxidation time 0–8 h	Removal of micropollutants and organics from WWTP RO concentrate	Total COD removal after 8 h treatment at 50 A/m², over 92 % removal of all pollutants after 2 h oxidation	Long 8 h oxidation time for total COD removal at applied current density of 50 A/m³, formation of trihalomethanes, energy consumption 59 kWh/kg COD removed (0.212 kJ/mg COD)/ 6.4 kWh/m³ at 50 A/m² current density	(Pérez et al., 2010)
	Ti/Pt-IrO₂ electrode, current density 100 A/m², electrical charge Q= 0.55 Ah/l, oxidation time 0–22 h	Removal of organics from WWTP RO concentrate	45% COD removal, 16% DOC removal, 57% DON removal, 74% color removal	Generation of oxidation by-products such as trihalomethanes and haloacetic acids, energy consumption <2.43 kWh/m³	(Bagastyo, Radjenovic, et al., 2011)
Solar photo-Fenton oxidation	3 m² compound parabolic collector solar pilot plant, H₂O₂ dose 50 mg/L, Fe(II) dose 0.1 mM, accumulated UV energy 7.5 kJ/L	Removal of micropollutants from WWTP NF concentrate (VRF 4)	>90% removal of all studied micropollutants (10–55,000 ng/L) such as caffeine, carbamazepine, naproxen and atenolol	Optimization of reagent consumption and reduction of total costs for oxidation process (estimated total costs 0.48 €/m³), energy consumption (90% pollutant removal) 3.5–7.5 kJ/L (1–2.1 kWh/m³)	(Miralles-Cuevas et al., 2017)

(continued)

Table 3. Continued.

AOP technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
UV/H$_2$O$_2$ and UV/ S$_2$O$_8$$^{2-}$ oxidation	UV irradiation with four 15 W low pressure mercury lamps (λ = 254 nm), UV fluence 1000 mJ/cm^2, H$_2$O$_2$ dose 170 mg/L, K$_2$S$_2$O$_8$ dose 960 mg/L	Removal of micropollu-tants from WWTP RO concentrate	>90, >99 and 75–80 removal of propranolol, sulfamethoxazole and carbamazepine (UV/H$_2$O$_2$); >99, >90 and 80–90 removal of propranolol, sulfamethoxa-zole and carbamazepine (UV/S$_2$O$_8$$^{2-}$)	Destruction of some micropollu-tants required significant amount of energy (up to 3000 mJ/cm^2 UV output)	(Yang et al., 2016)
UVC/H$_2$O$_2$	UVC irradiation (λ = 254 nm) with 39 W UV lamp (fluence rate 8.91 mW/cm^2), H$_2$O$_2$ dosage 3 mM	Removal of organics from WWTP RO concentrate and increasing biodegradability	37–46% COD removal, 25% DOC removal (1 h oxidation), bio-degradability increase from 5% to 23% (1 h oxidation)	Energy consumption (electrical energy per order to achieve DOC residual ≤15 mg/L) was 58.8 kJ/mg of DOC oxidized (342–344 kWh/m^3)	(Umar et al., 2014)
UVA/TiO$_2$ photocatalysis	UVA irradiation with 9 W UV lamp, Degussa P-25 TiO$_2$ catalyst (50 m^2/g BET surface area, cata-lyst dose 0.5 and 1 g/l), irradiation time 1 h	Removal of organics from WWTP RO concentrate	41% DOC removal (0.5 g/L cata-lyst), 49% DOC removal (1 g/ L catalyst)	Energy consumption 9.3 kJ/mg of DOC oxidized lower compared to sonolysis and electrochem-ical oxidation, however still limited removal efficiency	(Dialynas et al., 2008)
Sonolysis	Ultrasonic irradiation, fixed frequency 80 kHz, energy level 67.5 and 135 W, irradiation time 1 h	Removal of organics from WWTP RO concentrate	29% DOC removal at 67.5 W and 34% DOC removal at 135 W	Energy consumption 810 kJ/mg of DOC oxidized (correspond-ing value 16.7 kJ/mg for elec-trochemical oxidation)	(Dialynas et al., 2008)

efficient degradation of micropollutants from the concentrated membrane concentrate is hampered and requires more time and energy (Garcia-Segura, Keller, Brillas, & Radjenovic, 2015). In many cases, it can thus be unreasonable to target a very high removal rate of organic compounds using AOPs alone (Table 3). Therefore, removal of organic compounds prior to AOP e.g., by membrane filtration, coagulation with metal salts or by adsorption with activated carbon increases the AOP efficiency and purification efficiency overall (Dialynas et al., 2008; Reungoat et al., 2010; Umar et al., 2014). For instance, Acero et al. (2016) concluded that the hybrid process of coagulation (ferric chloride) and ozonation was a more efficient solution to remove micropollutants and effluent organic matter from NF concentrate of municipal wastewater treatment compared to stand-alone processes. Even partial oxidation in an advanced oxidation process (incomplete removal of organic compounds but increased biodegradability) can be sufficient if the aim is to recycle the concentrate to an activated sludge process. Another disadvantage of AOPs are harmful oxidation by-products potentially formed during oxidation, especially if the treated membrane concentrate contains a significant amount of chlorine based substances (Bagastyo, Radjenovic, et al., 2011; Pérez et al., 2010). The formation of hazardous trihalomethanes (THMs) or haloacetic acids (HAAs) is possible, when relatively saline concentrates are treated with an AOP such as electrochemical oxidation (Bagastyo, Radjenovic, et al., 2011; Pérez et al., 2010).

Traditional AOP processes can be energy-intensive and difficult to operate, as well as having a complex process design. Thus, new oxidation approaches are needed in order to improve the cost efficiency of AOPs and also increase their use at industrial scale (Bagastyo, Radjenovic, et al., 2011; Panorel et al., 2013; Umar et al., 2014). Of the most studied AOPs utilized for membrane concentrates, photocatalytic oxidation seems to be relatively energy efficient for dilute membrane concentrates (Dialynas et al., 2008). However, the oxidation reactions in photocatalytic oxidation can be slow (Panorel et al., 2011). In order to enhance the cost efficiency of AOPs, a non-thermal plasma method called pulsed corona discharge (PCD) has been developed (Panorel et al., 2013). In this process, strong oxidants such as short-living hydroxyl radicals and long-living ozone are generated *in situ* in a simple way. The PCD process has been reported to surpass the energy efficiency of ozonation by a factor of two in the oxidation of aqueous lignin, where an energy efficiency of 55 g/kWh was obtained by PCD versus the 7–25 g/kWh for ozonation (Panorel et al., 2011, 2013, 2014).

In the PCD process (Arola, Hatakka, Mänttäri, & Kallioinen, 2017), high voltage electrodes are used to ionize the liquid solution surrounding the electrode. A conductive region is thus formed where a discharge can be

released. High voltage pulse generators are used to create electric pulses that trigger the oxidation reactions occurring in the PCD reactor. Oxidation reactions can be enhanced by dispersing a water solution as water droplets through jets to improve contact with the electrode wire. The utilization of an oxygen atmosphere instead of air in the reactor also enhances the process efficiency as well as prevents the increase of nitrogen content to the treated solution. The PCD process has a proven efficiency for the degradation of pharmaceuticals from water as well as for the degradation of humic substances (Dobrin et al., 2013; Panorel et al., 2011, 2013). However, research related to PCD has thus far been done mainly with model solutions (Dobrin et al., 2013; Panorel et al., 2011, 2013), although promising results have been obtained recently from the PCD treatment of real MBR permeate and NF concentrate (Arola, Kallioinen, et al., 2017; Arola, Hatakka, et al., 2017; Arola, Kallioinen, & Mänttäri, 2015). Arola, Kallioinen, et al. (2017) utilized PCD oxidation (840 pulses per second, 0.3–10 kWh/m^3 oxidation energy, 89% O$_2$ atmosphere) to treat real NF concentrate (VRF 300) from municipal wastewater treatment. Over 92% degradation for pharmaceuticals diclofenac, carbamazepine, citalopram and furosemide was reached in the PCD oxidation (oxidation energy 10 kWh/m^3) of NF concentrate and oxidation increased the biodegradability of the concentrate 3.7 times based on BOD$_7$/COD ratio. Despite the moderate research experience acquired with real wastewater effluents, the potential of PCD oxidation for the treatment of membrane concentrates containing a significant amount of organic substances is evident.

4.3. Other treatment technologies

Technologies such as adsorption with activated carbon, for example, granular activated carbon (GAC) or pulvered activated carbon (PAC) adsorption (Acero et al., 2012; Dialynas et al., 2008; Gerrity et al., 2011; Lee, Ng, Ong, Hu, et al., 2009; Reungoat et al., 2010; Zhao et al., 2012), and coagulation with metal salts, mainly as ferric chloride (FeCl$_3$) and aluminum sulfate (Al$_2$(SO$_4$)$_3$) (Bagastyo, Keller, et al., 2011; Dialynas et al., 2008; Umar et al., 2014; Wert et al., 2011), have been studied as advanced treatment methods for the removal of organic and inorganic compounds in membrane concentrates (Table 4). Also other technologies such as electrocoagulation, capacitive deionization, ion exchange and various crystallization technologies has been examined as potential treatment option for municipal wastewater treatment effluents such as membrane concentrates (Bottini & Rizzo, 2012; Chung et al., 2017; Lahav et al., 2013; Lee, Ng, Ong, Tao, et al., 2009; Randall, Nathoo, & Lewis, 2011; Sanciolo et al., 2012).

Table 4. Examples of adsorption and coagulation processes for the treatment of membrane concentrates from municipal wastewater treatment.

Treatment Technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
Granular activated carbon adsorption (GAC)	GAC dosage 0.1–5 g/L, adsorption time 4 d, mixing speed 180 rpm, room temperature	Removal of organics from RO concentrate	91.3% removal of DOC (5 g/L dosage)	High dosage of carbon needed (5 g/L) for high retention of organics	(Dialynas et al., 2008)
Biological activated carbon adsorption (BAC)	BAC column, empty bed contact time 60 min, T = 30 °C	Removal of organics from RO concentrate and increasing the recovery rate	17–30% removal of DOC (62–78% when coupled with ozone 6 mg O_3/L); 14–49% removal of COD (80–98% when coupled with ozone 6 mg O_3/L)	Modest efficiency as a single unit (≤30% removal of DOC), major increase in efficiency when coupled with ozone treatment	(Lee, Ng, Ong, Hu, et al., 2009)
FeCl$_3$ coagulation	FeCl$_3$ dosage 10–30 mg/L, rapid mixing 100 rpm 2 min, 30 rpm for 20 min, settling 30 min, filtration through 1.5 μm and 0.7 μm microfiber filter	Removal of organics from RO concentrate and pretreatment for ozonation	10–47% removal of DOC	Poor removal efficiency for pharmaceuticals (removal rate <20%)	(Wert et al., 2011)
Al$_2$(SO$_4$)$_3$ coagulation	Al$_2$(SO$_4$)$_3$ dosage 1.5 mM as Al^{3+}, rapid mixing 250 rpm 2 min, 30 rpm for 30 min, settling 2 h, supernatant for analyses	Removal of organics from RO concentrate and pretreatment for AOP	16–29% removal of DOC, 17–29% removal of COD	Modest removal efficiency of organic compounds (<30% removal of DOC and COD)	(Umar et al., 2014)
Al$_2$(SO$_4$)$_3$ and FeCl$_3$ coagulation	Al$_2$(SO$_4$)$_3$ dosage 0.15–4.5 mM as Al^{3+}, FeCl$_3$ dosage 0.37–2.22 mM as Fe^{3+}, rapid mixing 210 rpm 2 min, 40 rpm for 15 min, 45–60 min settling, supernatant for analyses	Removal of organics from RO concentrate	17–34% removal of COD (alum), 41–49% removal of COD (iron), 25 and 38% removal of DOC (alum and iron, 1.5 mM and 1.48 mM)	Average removal efficiency especially for alum (<35% removal of COD and DOC)	(Bagastyo, Keller, et al., 2011)
Electrocoagulation and FeCl$_3$ coagulation	Rectangular flow-through electrocoagulation reactor, mild steel electrodes (900 cm^2), current density 8 mA/cm^2, iron dose 4 mM, FeCl$_3$ coagulation (iron dose 4 mM)	Removal of silica from synthetic RO concentrate	76–89% removal of silica with electrocoagulation (iron dose 4 mM) 64% removal of silica with FeCl$_3$ coagulation (iron dose 4 mM)	Efficiency of electrocoagulation for silica removal highly pH dependent	(Chen et al., 2017)
Main treatment technology	**Process properties**	**Reasons for use**	**Efficiency**	**Challenges**	**Reference**
NF + Magnesium ammonium phosphate (MAP) crystallization	Crystallization of NF concentrate (59–62 mg/L of P) from NF of treated municipal wastewater (flux in NF not reported, energy consumption estimate 0.6 kWh/m^3) in a separate MAP reactor where magnesium is added	Recovery of phosphorus as magnesium ammonium phosphate (struvite) from WWTP NF concentrate	Phosphorus recovery rate 70–80 % (corresponding 42–48 mg/L of P from NF concentrate)	High energy consumption (260 kWh/kg of P recovered) compared to the recovery from phosphate rock (55 kWh/kg)	(Bradford-Hartke et al., 2012)

(continued)

Table 4. Continued.

Treatment Technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
MBR+NF+EPR process (electrochemical phosphate recovery)	MBR with Kubota flat sheet module (0.04 μm pore size, constant flux 15 L/m²h), Dead-end Amicon filter for NF (0.0044 m² membrane area, 5 bar operating pressure, NF245 membrane from DOW, flux not reported), EPR cell having two acrylic glass chambers with platinum anode and steel cathode, electrode area 0.0022 m²/electrode, electrical current 10–50mA, Voltage 3 V, Fumasep FKS cation exchange membrane	Recovery of phosphorus from WWTP NF concentrate (13–33 mg/L of P)	>70% phosphorus recovery rate (temporarily >90%) was high compared to the commercial Crystalactor® process (65–70%), estimated energy costs 303 €/t of P recovered low compared to recovery from phosphate rock (685 €/t), no chemical addition in actual phosphorus recovery	Limited concentration of phosphorus in NF concentrate after Amicon filtration, VRF value only 3–4	(Kappel et al., 2013)
MBR+RO+PLE (polymeric ligand exchanger)	Kubota MBR, two stage RO unit with Saehan BLR RO membranes (fluxes from membrane processes not reported), DOW 3N Cu(II) loaded phosphate selective PLE resin, PLE column with 1.1 cm diameter, particle size 0.3–0.6 mm, column length 15.5 cm, empty bed contact time (EBCT) 8.5 min, regeneration of PLE column with 6% NaCl solution, pH 4.3, EBCT 27 min, struvite recovery from regenerant solution by adding NH_4Cl and $MgCl_2$ at Mg^{2+}:NH_4^+:P molar ratio of 1.5:1:1 at pH of 9	Recovery of struvite from WWTP RO concentrate (10 mg/L of P)	Nearly 100% precipitation of struvite from regenerant solution (containing around 78 mg/L of P_{tot}), struvite is estimated to be efficient fertilizer: 1 kg of struvite is enough to fertilize 2.6 ha of arable land as an application rate of 40 kg P as P_2O_5/ha/year	Overall rather complex process with many chemical additions, scale up into feasible industrial scale process	(Kumar et al., 2007)
UF+RO+Induced precipitation of phosphate (calcite seeds and NaOH)	UF pretreatment for RO, RO with BW30LE membranes (fluxes not reported), Batch precipitation (3.1–22.5 mM NaOH, Calcite seeds, 2 h at 250 rpm, filtration of samples with 0.45 μ filter)	Precipitation of phosphate from WWTP RO concentrate (1.3 mg/L of P)	Nearly 100% precipitation (analysis limits) of phosphate from RO concentrate (6.3 mM NaOH, pH 9.2)	Unselective precipitation at high pH values (precipitation of $Mg(OH)_2$ at pH > 10.5)	(Sperlich, Warschke, Wegmann, Ernst, & Jekel, 2010)
Membrane distillation (MD)	Direct contact membrane distillation, hydrophobic PTFE flat sheet membrane (0.004 m², 0.2 μm), flux between 12 and 16 kg/m²h, RO concentrate heated to 55 °C	Enhancement of RO process recovery rate and concentration of ions (PO_4^{3-}, Ca^{2+}, Mg^{2+}) by MD treatment of RO concentrate	85% recovery for RO concentrate achieved and 99% ion retention (such as PO_4^{3-}, Ca^{2+}, Mg^{2+}) obtained in MD	MD membrane fouling, significant requirement for thermal energy	(Naidu et al., 2017)

(continued)

Table 4. Continued.

Treatment Technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
Sodium zeolite column and liquid-liquid membrane contactor	Sodium zeolite (800–1200 μm) packed in a glass column (10 cm length, 1.5 cm diameter), liquid-liquid membrane contactor using Liquid-Cel Extra Flow X30HF polypropylene hollow fiber membrane (pore size 0.03 μm, membrane surface area 1.4 m^2), stripping solutions 98% H$_3$PO$_4$ and 65% HNO$_3$	Recovery of ammonia from ammonia concentrates (2–3 g NH$_3$/L, produced by zeolites from tertiary municipal wastewater effluents)	98% recovery rate of ammonia and ammonia recovery as diammonium phosphate (20–50 g/L)	Relatively strong feed solution (preferably ≥1 g NH$_3$/L) required for membrane contactor process	(Sancho et al., 2017)
Hybrid microfiltration-forward osmosis membrane bioreactor process (MF-FOMBR)	Cellulose triacetate FO membrane (0.072 m^2, flux 4.1–5.2 L/m^{2}h), PVDF microfiltration membrane (<0.1 μm pore size, 0.009 m^2, flux 4.6–9.3 L/m^{2}h) and recovery of phosphorus from MF permeate with precipitation reactor (NaOH dose to pH 9, constant stirring 100 rpm)	Recovery of phosphorus from municipal wastewater sludge	99% retention of NH$_4^+$-N and 98% retention of phosphate PO$_4^{3-}$-P in FO, >90% recovery of phosphorus as calcium phosphate in the precipitation reactor	Salt accumulation into the bioreactor, strong draw solution required for FO process	(Qiu et al., 2015)
ED + Pellet reactor for crystallization of calcium phosphate	ED with PC-SA anion exchange, PC,MVA monovalent selective anion exchange and PC-SK cation exchange membranes, 46.9 A/m^2 current density and product pH of 12. Crystallization in a pellet reactor, garnet sand 150–300 μm, pH 11, inlet phosphate concentration 2.5 mM, Ca/P molar ratio 1.5 and superficial velocity 61 m/h	Recovery of calcium phosphate from synthetic wastewater	Phosphate concentration from 7 mM to 16 mM with electrodialysis (44% phosphorus purity in ED product), 82.7% precipitation efficiency of calcium phosphate in the crystallization	Significant pH adjustment, process feasibility for real wastewater or membrane concentrates not investigated	(Tran et al., 2014)
ED + struvite reactor + gas stripping	Lab scale ED with JCM-II-07 cation exchange membranes and JAM-II-07 anion exchange membranes, constant 62 V voltage, current 0–2 A. 2 L struvite reactor, flow rate 10 mL/min, pH 9. Gas stripper including jacket heating, blower (gas flow 100 L/h) and nitric acid for fixation of ammonia, temperature 40 °C	Recovery of ammonium and phosphorus from synthetic anaerobic digestion effluent (200 mg/L Ptot, 600 mg/L Ntot)	96–100% removal of ammonia and 86–94% removal of phosphate salts in ED integrated with struvite reactor and ammonia stripping	Process feasibility for real wastewater or membrane concentrates not investigated	(Wang et al., 2015)

4.3.1. Adsorption and coagulation processes

Activated carbon treatment (Table 4) has been reported to be an efficient method for the removal of micropollutants and other organic compounds from municipal wastewater treatment effluents (Acero et al., 2012; Dialynas et al., 2008; Gerrity et al., 2011). Acero et al. (2012) obtained 65% removal of caffeine and 90% removal of diclofenac from secondary effluent using PAC adsorption with a carbon dose of 20 mg/L, and (Gerrity et al., 2011) obtained >99% removal of carbamazepine and diclofenac from secondary effluent using biological activated carbon adsorption (BAC) with a Filtrasorb F-400 carbon adsorption column (flow 40 L/min, 570 kg of carbon, 5 month operation). According to Dialynas et al. (2008) and Acero et al. (2012), high dosages of activated carbon are usually needed to attain high removal rates for organic compounds. In GAC adsorption of a reverse osmosis concentrate containing 10 mg/L of DOC (∼31 mg/L of COD based on COD/DOC factor 3.1 estimated from Table 1), 5 g/L of carbon was required to attain over 90% DOC removal (Dialynas et al., 2008). This dose of GAC would be equal to 5 kg of carbon/m^3 of concentrate, which could cost around 1.9–4.9 \$/m^3 of concentrate (Alibaba.com, 2018a). In a study by (Acero et al., 2012), 0.6 g/L PAC dose was required for over 85% removal of COD from a secondary effluent containing 22.4 mg/L of COD corresponding to DOC value of 7.2 mg/L (DOC times 3.1 equals COD, Table 1). This PAC dose (0.6 kg/m^3) could cost around 0.5–0.7 \$/m^3 of effluent (Alibaba.com, 2018b). The cost of the adsorbent is a limiting factor utilization of GAC adsorption for treatment of membrane concentrates. Although a smaller amount of adsorbent is needed in PAC adsorption it is still a relatively expensive treatment. Another drawback with PAC adsorption is that the used adsorbent might be more challenging to regenerate compared to GAC (more energy required for the regeneration process), which means that more solid waste may be produced.

Other adsorbents such as carbon capsules encapsulated with magnetite nanoparticles (Zhang et al., 2011) and tannin rigid foams (Sánchez-Martín, Beltrán-Heredia, Delgado-Regaña, Rodríguez-González, & Rubio-Alonso, 2013a, 2013b) have also been examined as potential adsorbents for wastewater treatment. Zhang et al. (2011) tested mesoporous carbon capsules encapsulated with magnetite (Fe_3O_4) nanoparticles as an alternative to activated carbon for removal of organic pollutants (dyes and phenol) from aqueous solutions. Mesoporous carbon capsules proved to be a more effective adsorbent for the removal of phenol from phenol-water solution compared to activated carbon. A maximum adsorption capacity of 108.4 mg of phenol/g of adsorbent could be reached by using mesoporous carbon capsules as an adsorbent (61.1 mg of phenol/g of absorbent by using activated carbon). An enhanced adsorption efficiency compared to the traditional

activated carbon was identified to be a combined result of mesoporous carbon capsules and magnetic core (Fe_3O_4). Carbon capsules provided very high surface area and large pore volume and magnetic core enabled the particles to be isolated efficiently from the mixture by applying external magnetic field. (Sánchez-Martín et al., 2013a) utilized tannin rigid foam as an adsorbent to remove micropollutant trimethoprim from an aqueous trimethoprim solution. A high adsorption capacity of 25 mg of trimethoprim/ g of adsorbent was reached in the adsorption tests with tannin rigid foam, which was comparable to other commercial adsorbents already used in wastewater treatment. Although mesoporous carbon capsules and tanning rigid foams show promising adsorption capabilities (Sánchez-Martín et al., 2013a; Zhang et al., 2011), they have been tested only with aqueous model solutions, which is a very different situation compared to the use in real municipal wastewater or even in membrane concentrates from municipal wastewater treatment. Thus, based on the available information, strong conclusions on the potentiality of these adsorbents for the treatment of membrane concentrates from municipal wastewater treatment cannot yet be drawn.

Coagulation with iron ($FeCl_3$ or $FeSO_4$) or aluminum salts ($Al_2(SO_4)_3$) traditionally used for phosphorus removal from municipal wastewater has also been used in several studies (Bagastyo, Keller, et al., 2011; Umar et al., 2014; Wert et al., 2011) to remove organic substances from membrane concentrates of municipal wastewater treatment or as a pretreatment for advanced oxidation (Table 4). Coagulation with iron or aluminum salts can efficiently remove inorganic compounds such as phosphorus from membrane concentrates, but the removal efficiency for organic compounds, particularly pharmaceuticals, is only moderate (Table 4). Thus, to ensure sufficient removal of micropollutants and other organic substances, coagulation is usually coupled with other membrane concentrate treatment methods such as ozone or UV and hydrogen peroxide based AOP (Umar et al., 2014; Wert et al., 2011). The potential of traditional coagulation with iron or aluminum salts would appear to be limited because of clear disadvantages such as the change in pH of the water (requirement for further pH adjustment to compensate pH decrease). Coagulation also produces inorganic sludge, which is difficult to process, for instance, by incineration, oxidation or biological treatment.

Electrocoagulation (EC) is an electrochemical technology, which uses an electrochemical cell applied with a direct current voltage to remove substances such as phosphorus, nitrate, sulfate or silica from wastewater or membrane concentrate (Kumar & Chopra, 2015; Nguyen et al., 2016; Top, Sekman, Hoşver, & Bilgili, 2011; Tran, Drogui, Blais, & Mercier, 2012; Wan & Chung, 2015). An EC cell is equipped usually either with iron or

aluminum electrodes, which provides metal ions for coagulation process (ions detached from the electrodes), and water or wastewater is used as electrolyte (Nguyen et al., 2016). Electrocoagulation offers several advantages over traditional coagulation such as simple and easy operation, short retention time and lower sludge production (Nguyen et al., 2016; Top et al., 2011). Tran et al. (2012) tested electrocoagulation as a tertiary treatment to remove phosphorus from municipal wastewater spiked with different phosphorus concentrations (initial P_{tot} concentration 5–50 mg/L). They used a batch electrolytic reactor made of acrylic material with eight parallel mild steel plate electrodes (110 cm^2/each) and direct current power source (maximum current 70 A, open circuit potential 40 V) with constant current density (12–95 mA/cm^2) to remove phosphorus. The best removal rates ($\geq$97%) were reached by combining electrocoagulation at optimum conditions (38.2 mA/cm^2 current density, 20 min treatment time) with flocculation (cationic polymer 10 mg/L). The initial phosphorus concentration did not have an influence on the phosphorus removal. The total cost for the tertiary electrocoagulation and flocculation at optimum conditions was estimated to be between 0.24–0.35 \$CAN/m^3 (0.16–0.23 €/m^3) of treated effluent. Chen et al. (2017) compared electrocoagulation with mild steel electrodes and chemical coagulation with FeCl$_3$ for the removal of dissolved silica from synthetic HERO process concentrate (SiO$_2$ 1000 mg/L, Na$^+$ 1490 mg/L, Cl$^-$ 400 mg/L). Electrocoagulation was performed with a rectangular flow-through reactor equipped with nine mild steel electrodes (total anode surface area 900 cm^2) by using a constant current density of 8 mA/cm^2. 76–89% silica removal from membrane concentrate (pH 5–7.5) was achieved with electrocoagulation by using an iron dose of 4 mM, which was significantly higher compared to 64% obtained from chemical coagulation with FeCl$_3$ (iron dose 4 mM, concentrate final pH 3). The difference in the silica removal between EC and chemical coagulation was explained by the pH difference in the concentrate during coagulation treatment (low pH decreases silica removal). The pH decrease in EC was more modest compared to chemical coagulation (same iron dose), since in the EC process the part of the acid formed via precipitation of Fe(OH)$_3$ was consumed in the cathode reaction of hydrogen gas evolution ($2H^+ + 2e^- \rightarrow H_2$).

Traditional coagulation can be an effective method to remove inorganic compounds, whereas activated carbon adsorption can be used mainly to remove organic compounds from the membrane concentrates. However, since the cost of adsorbent or the waste formed in these processes pose challenges, a possible approach could be their application mainly as a pretreatment method for concentrates that are difficult to treat directly with membrane filtration or advanced oxidation. However, if the aim is nutrient recovery from membrane concentrate, the addition of chemicals, such as

coagulants or adsorbents, to the membrane concentrate could be avoided to prevent formation of tightly bound metal salts, which may not be as readily utilized as fertilizers for plants. In addition, fractions produced by coagulation or adsorption need to be separated from the concentrates and reused, if possible, in order to prevent unnecessary waste generation. For instance, activated carbon can be reused after proper regeneration by either thermal or chemical methods. However, a challenge in thermal regeneration can be high capital costs and the carbon losses involved, and chemical regeneration produces a solvent solution containing impurities, which then has to be treated. By using electrocoagulation instead of chemical coagulation the use of excess chemicals can be avoided (overdosing may occur often in traditional coagulation) and the production of inorganic sludge can be decreased (Nguyen et al., 2016; Top et al., 2011). However, further research is needed for electrocoagulative treatment of real membrane concentrates before the feasibility of electrocoagulation technology for membrane concentrates can be confirmed.

4.3.2. Ion exchange and capacitive deionization

Ion exchange processes have been utilized in municipal wastewater treatment to remove organic matter, recover phosphorus or concentrate ammonium (Bottini & Rizzo, 2012; Malovanyy, Sakalova, Yatchyshyn, Plaza, & Malovanyy, 2013; Nguyen et al., 2011). In the ion exchange process the ions in the solution to be treated are displaced by ions of similar charge, which are released from the surface of an insoluble material (ion exchange resin) or in the magnetic ion exchange the displacing ions are released from the magnetic resins having magnetic components such as γ-Fe_2O_3 (Bottini & Rizzo, 2012; Nguyen et al., 2011). Bottini and Rizzo (2012) utilized ion exchange with an anionic iron oxide resin (LayneRT resin, packed bed column test, flow rate 6.5 cm^3/min, empty bed contact time 5.7–5.8 min) to recovery phosphorus from urban wastewater treatment plant sludge liquor (pH 8, 776 mg/L COD, 475 mg/L PO_4^{3-}). A maximum adsorption capacity of 14.2 and 14.4 mg P/g of iron oxide resin could be achieved from sludge liquor with new and regenerated resins. A total recovery efficiency of 95% for phosphorus from sludge liquor could be achieved in the regeneration step (1 M NaOH, less than 13 bed volumes) of ion exchange process (Bottini & Rizzo, 2012). Malovanyy et al. (2013) studied the concentration of ammonium from municipal wastewater (pH 7.4–7.8, alkalinity 5.7 mmol/L, NH_4-N 27 mg/L) with ion exchange process utilizing the SAC resin KU-2-8 (11.1 g sulfonated polystyrene type resin, packed bed column test, bed height 403 mm, bed volume 30.5 mL, flow rate 24–33 bed volumes per hour, empty bed contact time 1.8–2.5 min). By using 10 g/L NaCl as a regenerant, an ammonium concentration of

187–367 mg/L was achieved. A higher NaCl concentration of 30 g/L enabled even higher ammonium concentration (445–581 mg/L). Over 96% ammonium removal efficiency could be reached in the ion exchange treatment of municipal wastewater (Malovanyy et al., 2013). As presented above, ion exchange can be an efficient technology to concentrate nutrients from municipal wastewater. However, the technology is not completely selective (concentrates also organic substances) and requires a strong regeneration solution. Furthermore, only limited research has been conducted with real municipal wastewater treatment effluents let alone membrane concentrates.

Lee, Ng, Ong, Tao, et al. (2009) studied capacitive deionization (CDI) as an approach for the removal of dissolved solids, salts and organic compounds from reverse osmosis concentrates. CDI is a low-pressure electrochemical process utilizing electrical field to remove dissolved ions from an electrolyte stream. Process occurs in three phases, purification, regeneration and purge. During purification, an electrical field (potential difference 1.2–1.5 V) between two electrodes makes the ions to move towards oppositely charged electrodes where the ions are electrosorbed in the so-called electrical double layer. By reversing the potential difference between electrodes, ions are released from the electrodes and flushed out of the CDI cell in a stream with a high salt concentration. Bench-scale CDI system with a flow rate of 250 mL/min, electrode surface area of $0.7\,m^2$ and voltage of 1.3 V was used to treat RO concentrate of a water reclamation plant reclaiming secondary effluent. The CDI process was able to remove over 88 and 87% of total dissolved solids (TDS) and ions (such as Na^+, K^+, Ca^{2+}, Cl^-), 52–81% of phosphate (PO_4^{3-}) and 50–63% of total organic carbon (TOC). It was found that fouling of the CDI electrodes can limit utilization of this deionization technology (Lee, Ng, Ong, Tao, et al., 2009). Membrane concentrate treatment with CDI may also be unattractive if the aim is to recover nutrients from concentrates, since CDI removes also other ions and solids from the concentrate along with the phosphates.

4.3.3. Crystallization technologies

Several crystallization technologies such as evaporation crystallization, cooling crystallization, reactive crystallization and seed accelerated crystallization have been studied as potential technologies to enhance the water recovery rates or to recover salts or nutrients from municipal wastewater effluents such as membrane concentrates (Berg, Knoll, Kaschka, Weidler, & Nüesch, 2007; Berg et al., 2005, 2006; Fernández-Torres, Randall, Melamu, & von Blottnitz, 2012; Lahav et al., 2013; Lee, Weon, Lee, & Koopman, 2003; Lu et al., 2017; Sanciolo et al., 2012; Sanciolo, Zou, Gray, Leslie, & Stevens, 2008; Tran et al., 2012, 2014). In evaporation crystallization, a heat treatment is used to detach the solvent from the solute and solute starts to

crystallize in the form of solid state crystals. Initially the solution is unsaturated at a given temperature and external heat source is used to gradually heat the solution and remove the solvent. Solvent gradually evaporates from the solution and saturation point is reached after which crystallization of the solute occurs. Multi-effect evaporation crystallization and mechanical vapor recompression crystallization are the two main types of evaporation crystallization (Lu et al., 2017). Cooling crystallization is typically utilized for solutions in which the solubility of solute have strong dependence of the temperature. Usually, solubility of many chemical compounds decreases by decreasing temperature of the solution. These compounds can be crystallized by cooling the solution under feasible conditions. Cooling crystallization can be divided into three different techniques: solute crystallization, freezing crystallization and eutectic freeze crystallization (Lu et al., 2017).

In reactive crystallization a poorly soluble or insoluble substances are created via reactions between a gas and a solution or between two solutions. In reactive crystallization, the crystallization usually occurs under highly supersaturated conditions and primary nucleation dominates over secondary nucleation. Crystallization usually starts right after the solutions are mixed since the supersaturation level is high. Reactive crystallization can produce high purity products and therefore, it has been often used to separate and recover heavy metal ions or nutrient ions such as NH_4^+ and PO_4^{3-} from the wastewater treatment effluents (Lu et al., 2017). In seed accelerated crystallization or precipitation a seed material such as calcium carbonate or tobermorite rich calcium silicate hydrate is used to facilitate and enhance the crystallization process (Berg et al., 2005, 2006, 2007; Sanciolo et al., 2008). Seed material is added to the solution to provide a nucleating site for precipitation of ions from supersaturated solution. The rate of accelerated crystallization is then dependent on the degree of supersaturation as well as the number of nucleating sites added to the solution (amount of seed material) (Sanciolo et al., 2008). Sanciolo et al. (2012) utilized accelerated seeded precipitation to enhance the water recovery in reverse osmosis by removing calcium scale precursors from RO concentrate (Ca 130 mg/L) of inland municipal wastewater desalination plant. By using calcium phosphate seeds (20 g/L) at pH 10, the calcium concentration in the concentrate could be reduced to below 10 mg/L. This seed accelerated precipitation of salts from the RO concentrate enabled an enhancement of the water recovery from 70% to 90%.

Randall et al. (2011) studied eutectic freeze crystallization (EFC) as a solution to recover salts from highly saline RO concentrate originating from the water reclamation plant. EFC is a novel method that can treat brines and concentrates to recover pure salt and water; in principle, this technology could also be used for dilute aqueous waste streams such as

membrane concentrates. In the EFC process, the solution containing dissolved contaminants is slowly frozen, causing ice crystals to form, and the contaminants concentrate slowly in the remaining solution. Eventually, these concentrated contaminants crystallize at a specific eutectic temperature. The ice crystals formed can be separated from the mother liquid by exploiting the density properties of the crystals and mother liquid. The ice crystals have lower density than mother liquor (<1 vs 1–$1.2\,g/cm^3$) and thus ice crystals can be recovered from the top of the reactor whereas the salt crystals have higher density (1.2–$1.7\,g/cm^3$) and can be recovered from the bottom of the reactor. Thus, pure water and pure salt can be obtained from the process (Lewis et al., 2010; Reddy, Lewis, Witkamp, Kramer, & van Spronsen, 2010). Randall et al. (2011) treated concentrated RO concentrate (conductivity $22\,mS/cm$, pH 6.5, Na^+ $6.7\,g/L$, Ca^{2+} $1.3\,g/L$, SO_4^{2-} $16\,g/L$) originating from high recovery RO plant (99% recovery of potable water) with EFC, which was able to convert 97% of the concentrate into pure water, pure calcium sulfate (98% purity) and sodium sulfate (96.4% purity).

Lahav et al. (2013) crystallised struvite from the liquid after centrifugation of municipal wastewater sludge using a fluidized bed reactor and NF concentrate from nanofiltration of ultrafiltered seawater as a magnesium source. Over 90% removal of phosphorus in the form of struvite (95% purity) was achieved by dosing a mixture of centrifuge supernatant (100–$300\,mg/L$ P_{tot}, 450–$600\,mg/L$ N_{tot}) and seawater NF concentrate rich in magnesium ($7\,g/L$) to the fluidized bed crystallizer operated at pH 7.6 or 8.1. The magnesium production for crystallization using seawater nanofiltration was estimated to be less than 50% of the cost of magnesium chemicals. An integrated approach of crystallization in a pellet reactor and electrodialysis to treat synthetic RO concentrate and wastewater has been examined by Tran et al. (2012, 2014). A lab scale electrodialysis cell with three pieces of PC-SA anion exchange membranes, three pieces of PC-MVA monovalent selective anion exchange membranes and four pieces of PC-SK cation exchange membranes ($0.0064\,m^2$ each) was used by Tran et al. (2014) to concentrate phosphate in synthetic wastewater. After concentration a crystallization of calcium phosphate from the solution was conducted in a pellet reactor (seed material garnet sand 150–$300\,\mu m$, initial pH 7–11, $CaCl_2.2H_2O$ solution dosing $1\,L/h$, flow rate 14–$22\,L/h$). Phosphate concentration could be increased from $7\,mM$ in the feed solution to $16\,mM$ (44% purity) by using electrodialysis with a current density of $46.9\,A/m^2$ and ED product pH of 12. The maximum precipitation efficiency of 82.7% was achieved in the crystallization of calcium phosphate from the concentrated ED product in pellet reactor at following conditions: pH 11, inlet phosphate concentration of $2.5\,mM$, Ca/P molar ratio 1.5 and

superficial velocity 61 m/h (flow rate 18 L/h). The integrated process of electrodialysis and crystallization in a pellet reactor was seen as promising method for phosphorus recovery from wastewater (Tran et al., 2014).

Crystallization technologies appear to be promising membrane concentrate treatment options even as a stand-alone technologies, if the properties of the concentrates (concentration of nutrients, salt content) are suitable; otherwise, crystallization can be integrated with other technologies such as electrodialysis.

5. Recovery of valuable components

The main opportunity for creating value from membrane concentrates of municipal wastewater treatment is to recover nutrients from phosphorus or ammonium rich membrane concentrates (Table 1). In some wastewater treatment plants it might also be feasible to recover salts instead of nutrients or together with nutrients (Badruzzaman et al., 2009; Bradford-Hartke et al., 2012; Drenkova-Tuhtan et al., 2013; Fernández-Torres et al., 2012; Kappel et al., 2013; Kumar, Badruzzaman, Adham, & Oppenheimer, 2007; Lewis et al., 2010; Reddy et al., 2010; Zhang et al., 2009).

5.1. Nutrient recovery

Possible methods for the recovery of nutrients from nanofiltration or reverse osmosis concentrates and other concentrated municipal wastewater treatment effluents based on literature are summarized in Table 5. These methods include, for instance, the use of electrochemical cells containing cation exchange membranes (EPR process) (Kappel et al., 2013), struvite (magnesium ammonium phosphate hexahydrate, MAP) crystallization (Bradford-Hartke et al., 2012) and an integrated membrane system using polymeric ligand exchange resins (Kumar et al., 2007). In addition, full scale technologies based on continuous crystallization of calcium phosphate or MAP in a fluidized bed reactor such as Crystalactor® process have been developed (Giesen, 1999). In the Crystalactor® process the phosphate crystal pellets are produced in a fluidized bed reactor from phosphorus rich wastewater (60–80 mg/L) by using sand as a seed material (Desmidt et al., 2015; Giesen, 1999). Other commercial scale phosphorus recovery techniques have been developed based on the formation and recovery of MAP from municipal wastewater in a fluidized bed or batch reactor (Desmidt et al., 2015). According to Desmidt et al. (2015) economically feasible recovery of phosphorus from a water phase requires a liquid with a phosphate concentration of 50–60 mg/L.

Table 5. Potential technologies used for the concentration and recovery of nutrients from membrane concentrates and other concentrated effluents of municipal wastewater treatment.

Main treatment technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
NF + Magnesium ammonium phosphate (MAP) crystallization	Crystallization of NF concentrate (59–62 mg/L of P) from NF of treated municipal wastewater (flux in NF not reported, energy consumption estimate 0.6 kWh/m^3) in a separate MAP reactor where magnesium is added	Recovery of phosphorus as magnesium ammonium phosphate (struvite) from WWTP NF concentrate	Phosphorus recovery rate 70–80 % (corresponding 42–48 mg/L of P from NF concentrate)	High energy consumption (260 kWh/kg of P recovered) compared to the recovery from phosphate rock (55 kWh/kg)	(Bradford-Hartke et al., 2012)
MBR + NF + EPR process (electrochemical phosphate recovery)	MBR with Kubota flat sheet module (0.04 μm pore size, constant flux 15 L/m^{2}h), Dead-end Amicon filter for NF (0.0044 m^2 membrane area, 5 bar operating pressure, NF245 membrane from DOW, flux not reported), EPR cell having two acrylic glass chambers with platinum anode and steel cathode, electrode area 0.0022 m^2/electrode, electrical current 10–50 mA, Voltage 3 V, Fumasep FKS cation exchange membrane	Recovery of phosphorus from WWTP NF concentrate (13–33 mg/L of P)	>70% phosphorus recovery rate (temporarily >90%) was high compared to the commercial Crystalactor® process (65–70%), estimated energy costs 303 €/t of P recovered low compared to recovery from phosphate rock (685 €/t), no chemical addition in actual phosphorus recovery	Limited concentration of phosphorus in NF concentrate after Amicon filtration, VRF value only 3–4	(Kappel et al., 2013)
MBR + RO + PLE (polymeric ligand exchanger)	Kubota MBR, two stage RO unit with Saehan BLR RO membranes (fluxes from membrane processes not reported), DOW 3N Cu(II) loaded phosphate selective PLE resin, PLE column with 1.1 cm diameter, particle size 0.3–0.6 mm, column length 15.5 cm, empty bed contact time (EBCT) 8.5 min, regeneration of PLE column with 6% NaCl solution, pH 4.3, EBCT 27 min, struvite recovery from regenerant solution by adding NH$_4$Cl and MgCl$_2$ at Mg^{2+}:NH$_4$$^+$:P molar ratio of 1.5:1:1 at pH of 9	Recovery of struvite from WWTP RO concentrate (10 mg/L of P)	Nearly 100% precipitation of struvite from regenerant solution (containing around 78 mg/L of P$_{tot}$), struvite is estimated to be efficient fertilizer: 1 kg of struvite is enough to fertilize 2.6 ha of arable land as an application rate of 40 kg P as P$_2$O$_5$/ha/year	Overall rather complex process with many chemical additions, scale up into feasible industrial scale process	(Kumar et al., 2007)
UF + RO + Induced precipitation of phosphate (calcite seeds and NaOH)	UF pretreatment for RO, RO with BW30LE membranes (fluxes not reported), Batch precipitation (3.1–22.5 mM NaOH, Calcite seeds, 2 h at 250 rpm, filtration of samples with 0.45 μ filter)	Precipitation of phosphate from WWTP RO concentrate (1.3 mg/L of P)	Nearly 100% precipitation (analysis limits) of phosphate from RO concentrate (6.3 mM NaOH, pH 9.2)	Unselective precipitation at high pH values (precipitation of Mg(OH)$_2$ at pH > 10.5)	(Sperlich, Warschke, Wegmann, Ernst, & Jekel, 2010)

(*continued*)

Table 5. Continued.

Main treatment technology	Process properties	Reasons for use	Efficiency	Challenges	Reference
Membrane distillation (MD)	Direct contact membrane distillation, hydrophobic PTFE flat sheet membrane (0.004 m², 0.2 μm), flux between 12 and 16 kg/m²h, RO concentrate heated to 55 °C	Enhancement of RO process recovery rate and concentration of ions (PO_4^{3-}, Ca^{2+}, Mg^{2+}) by MD treatment of RO concentrate	85% recovery for RO concentrate achieved and 99% ion retention (such as PO_4^{3-}, Ca^{2+}, Mg^{2+}) obtained in MD	MD membrane fouling, significant requirement for thermal energy	(Naidu et al., 2017)
Sodium zeolite column and liquid-liquid membrane contactor	Sodium zeolite (800–1200 μm) packed in a glass column (10 cm length, 1.5 cm diameter), liquid-liquid membrane contactor using Liquid-Cel Extra Flow X30HF polypropylene hollow fiber membrane (pore size 0.03 μm, membrane surface area 1.4 m²), stripping solutions 98% H_3PO_4 and 65% HNO_3	Recovery of ammonia from ammonia concentrates (2–3 g NH_3/L, produced by zeolites from tertiary municipal wastewater effluents)	98% recovery rate of ammonia and ammonia recovery as diammonium phosphate (20–50 g/L)	Relatively strong feed solution (preferably $\geq$1 g NH_3/L) required for membrane contactor process	(Sancho et al., 2017)
Hybrid microfiltration-forward osmosis membrane bioreactor process (MF-FOMBR)	Cellulose triacetate FO membrane (0.072 m², flux 4.1–5.2 L/m²h), PVDF microfiltration membrane ($\leq$0.1 μm pore size, 0.009 m², flux 4.6–9.3 L/m²h) and recovery of phosphorus from MF permeate with precipitation reactor (NaOH dose to pH 9, constant stirring 100 rpm)	Recovery of phosphorus from municipal wastewater sludge	99% retention of NH_4^+-N and 98% retention of phosphate PO_4^{3-}-P in FO, >90% recovery of phosphorus as calcium phosphate in the precipitation reactor	Salt accumulation into the bioreactor, strong draw solution required for FO process	(Qiu et al., 2015)
ED + Pellet reactor for crystallization of calcium phosphate	ED with PC-SA anion exchange, PC,MVA monovalent selective anion exchange and PC-SK cation exchange membranes, 46.9 A/m² current density and product pH of 12. Crystallization in a pellet reactor, garnet sand 150–300 μm, pH 11, inlet phosphate concentration 2.5 mM, Ca/P molar ratio 1.5 and superficial velocity 61 m/h	Recovery of calcium phosphate from synthetic wastewater	Phosphate concentration from 7 mM to 16 mM with electrodialysis (44% phosphorus purity in ED product), 82.7% precipitation efficiency of calcium phosphate in the crystallization	Significant pH adjustment, process feasibility for real wastewater or membrane concentrates not investigated	(Tran et al., 2014)
ED + struvite reactor + gas stripping	Lab scale ED with JCM-II-07 cation exchange membranes and JAM-II-07 anion exchange membranes, constant 62 V voltage, current 0–2 A. 2 L struvite reactor, flow rate 10 mL/min, pH 9. Gas stripper including jacket heating, blower (gas flow 100 L/h) and nitric acid for fixation of ammonia, temperature 40 °C	Recovery of ammonium and phosphorus from synthetic anaerobic digestion effluent (200 mg/L Ptot, 600 mg/L Ntot)	96–100% removal of ammonia and 86–94% removal of phosphate salts in ED integrated with struvite reactor and ammonia stripping	Process feasibility for real wastewater or membrane concentrates not investigated	(Wang et al., 2015)

MAP crystallization (Table 5) may be a feasible method for phosphorus recovery at elevated pH around 9, if there is a phase ratio around 1.2–1.6:1 between magnesium and phosphorus and 1–5:1 between ammonium and phosphorus in the membrane concentrate (Bradford-Hartke et al., 2012; Jaffer, Clark, Pearce, & Parsons, 2002; Matsumiya, Yamasita, & Nawamura, 2000; Negrea, Lupa, Negrea, Ciopec, & Muntean, 2010; Wang, Song, Yuan, Peng, & Fan, 2006). According to Jaffer et al. (2002) and Matsumiya et al. (2000), a suitable Mg/P ratio for a MAP crystallization process is between 1.3–1.5 and usually excessive amount of ammonia is available (ammonium to phosphorus ratio > 1) (Doyle & Parsons, 2002). The MAP crystallization technology requires usually an addition of a separate magnesium based chemical such as $MgCl_2$ to the NF or RO concentrate in a separate MAP reactor and phosphate in the concentrate will then crystallize into MAP (Bradford-Hartke et al., 2012). The presence of calcium ions disturbs the precipitation of MAP and the Ca/Mg ratio determines the crystallization to either calcium phosphate (calcium hydroxyapatite, HAP) or MAP (Bradford-Hartke et al., 2012). According to Bradford-Hartke et al. (2012), the Ca/Mg ratio should be below 1 in order to crystallize MAP instead of HAP.

Kappel et al. (2013) utilized a laboratory scale non-continuous EPR process to recover phosphorus from nanofiltration concentrate (Table 5), where the carbonates were stripped at the anode and phosphorus was recovered efficiently as calcium phosphate at the cathode (Table 5). In the process concept presented, no phosphorus precipitation chemicals were used in the MBR process. According to Kappel et al. (2013), the EPR process could also be operated continuously (Figure 5), which would enable a full scale EPR process. If a sufficient concentration of calcium ($\sim$100 mg/L) is present in the membrane concentrate, it is also possible to recover calcium phosphate by adding sodium hydroxide and precipitating the phosphorus at elevated pH (Desmidt et al., 2015; Kappel, 2014; Sperlich et al., 2010).

Polymeric ligand exchangers and induced precipitation can give nearly 100% phosphorus recovery as MAP or hydroxyapatite (HAP) (Table 5). MAP recovery with ligand exchangers is, however, a complex process and requires many chemical additions (Kumar et al., 2007). The challenge in the induced precipitation of hydroxyapatite (HAP) using calcite seeding (Table 5) on the other hand is the nonselective precipitation at high pH (Sperlich et al., 2010). Another method studied to recover calcium phosphate from wastewater (Table 5) is to use electrodialysis in combination with crystallization in a fluidized bed pellet reactor (Tran et al., 2014, 2015).

The commercial scale Crystalactor® process for calcium phosphate recovery from municipal wastewater using crystallization in a fluidized bed
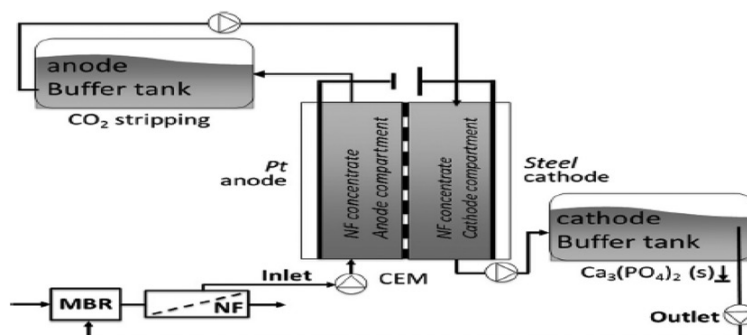
Figure 5. Schematic diagram of a continuous EPR process for phosphate recovery (Kappel et al., 2013).

reactor has reported to have a recovery rate of 65–72% for phosphorus, but it requires calcium hydroxide and seed material addition (Giesen, 1999; Woods, Sock, & Daigger, 1999). In crystallization of the calcium phosphate, an elevated pH is often used or calcium salts are added to the effluent to enhance the crystallization (De-Bashan & Bashan, 2004; Giesen, 1999; Kappel, 2014). However, even spontaneous crystallization is possible at neutral pH conditions, if the effluent contains a sufficient amount of phosphorus and calcium (Carlsson, Aspegren, Lee, & Hilmer, 1997). Carlsson et al. (1997) state that spontaneous crystallization of calcium phosphate is possible at neutral pH conditions if concentrations of 100 mg/L for calcium and 50 mg/L for phosphorus are exceeded.

5.2. Recovery of salts

In addition to nutrient recovery, the recovery of salts using for instance eutectic freeze crystallization (EFC) might be a possible approach, particularly in the treatment of reverse osmosis concentrates containing a high amount of salts (>1 g/L) (Randall et al., 2011). Concentrates of this kind are, for instance, reverse osmosis concentrates from desalination plants, and concentrates from the mining industry and metallurgical industry (Fernández-Torres et al., 2012; Lewis et al., 2010; Randall et al., 2011; Reddy et al., 2010). Fernández-Torres et al. (2012) reported efficient recovery of pure water and Na_2SO_4 (40 t/day) with three phase eutectic freeze crystallization of synthetic saline wastewater containing 4 wt. % Na_2SO_4. However, the membrane concentrates from municipal wastewater treatment often contain only moderate amount of salt forming ions such as Ca^{2+} (<0.6 g/L), Na^+ (≤0.8 g/L) and SO_4^{2-} (≤1.5 g/L) (Table 1). Thus the utilization of EFC technology for membrane concentrates from municipal wastewater treatment is probably limited to those few areas where saline wastewater is treated for instance due to strong presence of industry

discharging saline effluents to the municipal sewage network (Fernández-Torres et al., 2012; Lewis et al., 2010; Randall et al., 2011; Reddy et al., 2010). Examples of commercially available salts that could be potentially also recovered from the membrane concentrates of municipal wastewater are for instance $CaCl_2$, NaCl and Na_2SO_4. However the type of salts possibly to be recovered from the concentrates varies significantly and depends largely on the magnitude and type of industry (such as chemical or pulp and paper) discharging their effluents to the municipal sewage network. Therefore in most cases it is not economically viable to recover salts from membrane concentrates of municipal wastewater treatment due to the limited value of the salts and low concentrations of ions forming salts.

In addition to EFC technology, a similar freeze desalination technology called the HybridICE^{TM} process has been developed for the treatment of concentrated brines such as reverse osmosis concentrates from mining processes. In the HybridICE^{TM} process, the brine is cooled to a temperature where ice crystals will form from the water molecules present in the brine solution. Continuous extraction of pure water (ice) from the brine is achieved by circulating the brine in a closed circuit through scraped surface heat exchangers installed in series. Nucleation of crystals occurs in the first heat exchanger, while ripening happens in the second heat exchanger. This crystallization process is able to produce high purity crystals without using fresh water for ice crystal washing. The applicability of the HybridICE^{TM} process, as with the EFC process, is likely to be limited to membrane concentrates containing a high amount of salts (Mtombeni et al., 2013; Zvinowanda et al., 2014).

Other technologies such as electrodialysis metathesis (EDM), membrane crystallization and capacitive deionization (CDI) have also been used to remove and recover salts from membrane concentrates and other concentrated wastewaters. Zhang et al. (2017) utilized EDM in an integrated system of NF-EDM to synthesize high solubility salts by treating NF permeate from nanofiltration of synthetic wastewater as a monovalent stream (containing most of the monovalent ions) and NF concentrate (320–730 mg/L of Ca^{2+} and 2026–2770 mg/L of SO_4^{2-}) as a divalent stream (containing most of the divalent ions) in a EDM stack. High solubility salts $CaCl_2$ and Na_2SO_4 could be synthetized and concentrated up to 7.6 and 10.5 times (compared to initial concentrations in the feeds NF permeate and concentrate for EDM) into two separate product streams with EDM. Quist-Jensen et al. (2017) recovered over 75% of Na_2SO_4 from industrial wastewater containing 45–55 g/L of Na_2SO_4 by using membrane crystallization. As discussed in the section 4.1.3, the membrane crystallization is usually more applicable for industrial wastewaters containing significant concentration of salts. Thus the utilization of membrane crystallization for membrane

concentrates of municipal wastewater treatment might not be feasible in most cases due to limited concentration and value of salts present in the concentrate. Lee, Ng, Ong, Tao, et al. (2009) utilized capacitive deionization (CDI) for the removal of ions such as Na^+, K^+, Ca^{2+}, Cl^- and PO_4^{3-} from reverse osmosis concentrates. CDI process removed over 87% of Na^+, K^+, Ca^{2+} and Cl^- ions from the concentrate.

However, all technologies reviewed here require a relatively saline feed solution for a feasible operation. In addition, the salt products typically possible to recover from the membrane concentrates are low value products, which do not give economic incentives to carry out salt recovery. Thus, salt recovery from the membrane concentrates of municipal wastewater can be seen as attractive option only in plant sites, where saline wastewater is treated or in the cases where the salt content in the membrane concentrate is high.

6. Zero waste discharge

In the current environment of limited natural resources, it is important to aim towards minimal waste discharge and recirculation of e.g., nutrients from wastewaters, when designing new municipal wastewater treatment concepts. Near-zero waste discharge could be reached in municipal wastewater treatment with the technologies described in this review, if the nutrients are recovered with the processes described above and utilized, for example, as fertilizers, and residual concentrate from the nutrient recovery processes is recirculated to the biological wastewater treatment process. In case the membrane concentrate from municipal wastewater treatment would contain significant amount of salts, then the salts could be also recovered for instance by membrane crystallization or eutectic freeze crystallization as discussed previously in the sections 4.1.3 and 5.2. If concentrates contain high salt content then membrane crystallization or integrated membrane distillation crystallization can be a part of the solution towards zero waste discharge by recovering the salts from the concentrate (Chen, Lu, Krantz, Wang, & Fane, 2014; Tsai et al., 2017). Advanced oxidation can be applied to oxidize refractory compounds in the residual concentrate in order to increase their biodegradability and enable the recirculation to the biological process. Shear enhanced membrane filtration could potentially be applied, when necessary before actual nutrient recovery process to concentrate valuable nutrient ions and to increase the yield of pure water. Using these advanced treatment technologies, the quality of effluent to be discharged can also be considerably improved compared to traditional municipal wastewater treatment based on the activated sludge process. Therefore,

its reuse for e.g., irrigation purposes or even for the production of portable water is more attractive than purified wastewaters today.

To achieve zero-waste discharge in municipal wastewater treatment process the excess sludge formed in the biological purification process should also be utilized e.g., for agricultural purposes or incinerated. If the sludge and membrane concentrate is incinerated the utilization of ash is also required if entirely zero waste conditions and complete resource recycling in municipal wastewater treatment would be pursued. The ash produced in the incineration can be used in forest fertilizing as has been done with the membrane concentrate in the pulp and paper industry (Peinemann & Nunes, 2010).

7. Challenges

Conversion of membrane concentrates from voluminous waste streams to valuable components using advanced technologies such as tertiary NF/RO, shear enhanced membrane filtration, electrochemical phosphate recovery process (EPR), electrodialysis and advanced oxidation faces a number of challenges. Key challenges are related to the safety of the treated and discharged effluents, energy consumption and increased treatment costs, legislation related to wastewater treatment, as well as issues surrounding public acceptance of new processes and products.

7.1. Safety

Membrane concentrate from tertiary membrane filtration such as nanofiltration or reverse osmosis can be a problematic stream, since it may contain concentrated amounts of various hazardous micropollutants such as hormones, anti-inflammatory drugs (e.g., diclofenac) and mood drugs (e.g., carbamazepine), which can be detrimental for the aqueous environment (Abdelmelek et al., 2011; Li, Cabassud, Reboul, & Guigui, 2015; Pérez et al., 2010; Vieno & Sillanpää, 2014). Advanced oxidation can be used to degrade micropollutants and increase biodegradability of the concentrate and enable concentrate circulation back to biological processes. However, AOP must be used carefully, and optimized and operated correctly in order to prevent formation of potentially hazardous oxidation by-products such as trihalomethanes and haloacetic acids (Bagastyo, Radjenovic, et al., 2011; Pérez et al., 2010).

At present it is possible to spread activated sludge directly onto fields without sludge disinfection (European Commission, 2013; European Council, 1986). However, several European countries have implemented their own stricter regulations related to the utilization of activated sludge

for agricultural purposes and some countries such as the Netherlands have completely forbidden the utilization of untreated sludge for agricultural purposes and require the sludge to be treated by biological, chemical or thermal methods (European commission, 2015a; Kirchmann, Börjesson, Kätterer, & Cohen, 2017; Milieu Ltd., 2010). Similarly, activated sludge is not used in Sweden on land for agricultural purposes due to the pressure coming from the Swedish Consumer Coalition (Eriksson, Christensen, Ejbye Schmidt, & Ledin, 2008). Although there is no direct legislation related to membrane concentrate disposal, similar rules as for activated sludge could be assumed to be applicable. The use of AOP to degrade the micropollutants could enable the spreading of the membrane concentrates on fields.

Another concern related to membrane concentrates are microplastics, which are concentrated by advanced membranes processes into the concentrate, if present in municipal wastewater effluents (no physical barrier for microplastics in the traditional activated sludge processes compared to MBR which retains them) (Bayo, Olmos, López-Castellanos, & Alcolea, 2016; Leslie, Brandsma, van Velzen, & Vethaak, 2017; Mason et al., 2016). Microplastics are small (<5 mm) plastic particles which pollute the aquatic environment and can be even found from the aquatic organisms, since aquatic marine organisms may easily ingest microplastics together with their food or through contaminated prey (Bayo et al., 2016; Leslie et al., 2017; Mason et al., 2016). Municipal wastewater treatment effluents have been identified as a major source for microplastics discharge, although most of the microplastics are removed during the treatment process (Bayo et al., 2016; Leslie et al., 2017; Mason et al., 2016). Mason et al. (2016) studied microplastics pollution from 17 different municipal wastewater treatment plants in USA (daily flows varying between 2350 to 382,000 m^3/day) and concluded that on average over 4 million microplastic particles were discharged per day per plant. Thus if the tertiary membrane filtration producing membrane concentrate follows traditional wastewater treatment the presence of microplastics in membrane concentrate is probable and has to be taken into account when considering further concentrate treatment.

Presence of antibiotic resistant pathogenic bacteria (ARB) in the municipal wastewater treatment plant effluents is also an emerging concern, since the presence of antibiotic resistant bacteria in discharged effluents and thus in aquatic environment may reduce the efficiency of traditional antibiotics used to cure bacterial infections (Ben et al., 2017; Neudorf et al., 2017; Rafraf et al., 2016; Wen, Yang, Duan, & Chen, 2016). Several studies have indicated that antibiotic resistant bacteria, resistant to common antibiotics like tetracycline, are present around the world at low concentrations (around 1.1×10^1 to 8.9×10^3 CFU/mL) in municipal wastewaters even in the final

discharged effluents. This may create a significant risk for the aquatic environment (fish and other aquatic organisms) (Ben et al., 2017; Neudorf et al., 2017; Rafraf et al., 2016; Wen et al., 2016). These ARBs are retained efficiently in membrane filtration (size exclusion) and thus elevated concentrations of ARBs may be present in membrane concentrates. The potential presence of ARBs has to be taken into account when considering the end use of concentrates for instance to fertilizer applications. In some cases, it may thus be safer to incinerate the membrane concentrate, potentially rich in ARBs, together with the sludge before utilizing it as a fertilizer.

Membrane concentrates may also contain small concentrations of harmful heavy metals such as lead and zinc (Malamis et al., 2012); however, minor concentrations of these heavy metals presumably do not cause a significant risk. The safety of the calcium phosphate potentially recovered from the membrane concentrate might be crucial for some end uses. In addition to fertilizer applications, calcium phosphate could also be theoretically used for pharmaceutical applications, due to beneficial effects on bone tissue, assuming, of course, that a very high purity is reached (Barrère, van Blitterswijk, & de Groot, 2006; Heaney, Recker, Watson, & Lappe, 2010; Zhao, Liu, Sun, & Zhang, 2011).

There are no major safety issues associated with the high quality water produced in advanced wastewater treatment such as membrane bioreactor process followed by tertiary NF or RO, since the purity in NF or RO permeates is very high (TOC $< 1\,mg/L$, $P_{tot} < 0.1\,mg/L$, $NO_3^- < 15\,mg/L$, $>95\%$ removal of micropollutants, no bacteria or viruses) (Cartagena, El Kaddouri, Cases, Trapote, & Prats, 2013; Dolar et al., 2012; Sahar et al., 2011).

7.2. Cost issues

The total energy consumption and thus energy costs of wastewater treatment will increase significantly, if processes such as tertiary membrane filtration, high shear membrane filtration and advanced oxidation are applied in wastewater and membrane concentrate treatment. According to the literature, a rough estimation for the combined total energy consumption of tertiary membrane filtration processes and advanced oxidation for instance would be over $2\,kWh/m^3$ (Bagastyo, Radjenovic, et al., 2011; Dialynas et al., 2008; Jaffrin, 2008; Kazner, 2011; Mehrjouei et al., 2014). However, some cost savings and new income streams could partially balance the increased energy costs, since the use of chemicals in wastewater treatment such as phosphorus precipitation chemicals could be decreased and nutrients in the form of calcium phosphate or struvite (MAP) could be recovered and sold (see Section 5). The purchase cost of iron based precipitation chemicals such as ferric sulfate, which is widely used in traditional wastewater

treatment plants, could be around 150 €/ton, according to Lignell et al. (2014). However, this depends on the location, chemical supplier and actual chemical to be used. The selling price estimation for pure calcium phosphate is around 1048 $/ton according to the Molbase Chemical Database (2016) and around 220–900 $/ton for MAP fertilizer (Molinos-Senante, Hernández-Sancho, Sala-Garrido, & Garrido-Baserba, 2011). However, the selling prices for these fertilizers obtained from the nutrient recovery processes of municipal wastewater treatment could be slightly lower especially in the case of calcium phosphate, since the achieved purities for nutrients might be lower than in the commercial products. Thus, the economic feasibility of using these advanced treatment steps might be challenging at current nutrient prices and average electricity prices of 0.12 €/kWh (excluding VAT) for non-household consumers in Europe (Eurostat, 2017). Cost savings from the redundancy of precipitation chemicals and profits from the selling of recovered nutrients would also be somewhat limited in the current market situation. Some income could potentially be generated, if the high quality permeate produced in NF/RO can be sold for reuse, for instance, as process or irrigation water.

7.3. Legislation

Numerous laws, directives and governmental guidelines regulate traditional municipal wastewater treatment, much of which would be fully or partly applicable to advanced wastewater and membrane concentrate treatment (EPA, 2013; European Commission, 2013; European Council, 1986; European Council, 1991). From the point of view of the adoption of novel approaches to wastewater treatment, a challenge for the current legislation is that it varies greatly depending on location (EPA, 2013; European Commission, 2013). The most important legislation relates to the utilization of sludge and nutrients such as phosphorus for fertilizer applications. On the European level, phosphorus must be removed efficiently from the wastewaters, according to European Council directive 91/271/EEC (European Council, 1991). However, these directives do not set any requirements for nutrient recovery. Directives regulating phosphorus removal allow the precipitation of phosphorus with relatively inexpensive iron or aluminum based coagulants to the activated sludge, which produce stable and strongly bound compounds such as iron phosphates (European Commission, 2013). The potential recovery of phosphorus from these compounds may be challenging at a commercial scale, and the compounds are not necessarily readily useful for plants (European Commission, 2013). According to Kirchmann et al. (2017) only 10% of the nitrogen in the activated sludge is present as ammonium nitrogen and

readily usable for plants. Similarly, only 10% of the total phosphorus is present in water soluble form and easily accessible by plants and rest is strongly bound to iron or aluminum due to chemical precipitation of phosphorus conducted in traditional wastewater treatment (Kirchmann et al., 2017). Thus current legislation does not promote the move from traditional technology towards advanced process solutions that could create new value from waste streams. Due to the wide utilization of iron and aluminum salts for phosphorus precipitation and the economic challenges related to nutrient recovery processes, commercial scale recovery of phosphorus either as calcium phosphate or MAP for fertilizer applications in municipal wastewater treatment has been somewhat limited (European Commission, 2013; Giesen, 1999). Nevertheless, some commercial applications such as the Crystalactor® process have found some use in wastewater treatment for instance in a Chinese chemical company for phosphate recovery (daily flow 3600–4800 m^3) (European Commission, 2013; Giesen, 1999; Royal Haskoning DHV, 2018).

Globally, there are no strict or unified guidelines or limits for micropollutants in discharge waters from municipal wastewater treatment. The European Medicines Agency (EMA) has made a recommendation of 100 ng/L for all kinds of pharmaceuticals in surface waters in the vicinity of sensitive discharge areas. However, this is only a recommendation and thus not legally binding (Sahar et al., 2011). The awareness of micropollutants in discharge waters has grown and the European Union has already made a priority list of hazardous substances. This list contains micropollutants such as diclofenac and hormones that are recommended to be monitored on a regular basis from municipal wastewater treatment plant effluents. It would appear probable that legislation related to wastewater treatment will be tightened in the near future, and this may improve the market position of the advanced membrane concentrate treatment technologies described in this review (European Commission, 2012; European Commission, 2015b; Loos et al., 2012; Ribeiro et al., 2015).

7.4. Approval of society

Public resistance to usage of the high quality water that is produced in advanced wastewater treatment can be expected to be relatively low, since acceptance already exists of processes such as the membrane based NEWater process used in Singapore for production of drinking water from municipal wastewater (PUB, 2011; Wintgens et al., 2005). It can also be assumed that even direct utilization of AOP treated concentrate for fertilizer applications would presumably be acceptable, since activated sludge from conventional treatment is already widely used as fertilizer (European

Commission, 2013). The main challenge is likely to be found in the need to overcome the resistance of change of local authorities, as well as the strong belief and trust of municipalities, water companies as well as consultant companies for traditional technology. The awareness of possible new processes can in some cases be relatively good, but gaining acceptance for major changes like the use of calcium phosphate based pharmaceutical products of which the raw material originates from membrane concentrates of municipal wastewater treatment is likely to be a very challenging task. In the short term, it is probably more acceptable and feasible to utilize nutrients recovered from membrane concentrates in fertilizer applications.

8. Concluding remarks

Various membrane filtration technologies are already widely used in water and wastewater treatment processes such as water reclamation. Concentrate produced in membrane filtration, such as nanofiltration or reverse osmosis, is usually a voluminous waste stream, the further treatment of which can be challenging. Currently (2018), potentially valuable components in these concentrates are usually not recovered and utilized. The aim of this critical review was to identify feasible membrane concentrate management strategies for concentrates originating from municipal wastewater treatment that not only minimize the amount of waste but also enable the recovery of valuable components, mainly nutrients such as calcium phosphate or magnesium ammonium phosphate hexahydrate (MAP). It was concluded that one single treatment technology is insufficient to enable advanced membrane concentrate treatment that meets the multiple goals set for concentrate treatment such as minimized amount of waste and recovery of valuable components, all this without risking any safety aspects. Thus, hybrid processes that could involve technologies such as shear enhanced membrane filtration, electrodialysis, advanced oxidation and nutrient recovery via precipitation/crystallization are required in order to convert membrane concentrates from waste to value.

Based on this review, electrodialysis processes or shear enhanced membrane filtration in the form of nanofiltration or reverse osmosis with VSEP or CR filters could be potential options to concentrate the valuable components in membrane concentrate. Based on the literature a few technologies were seen as promising for value component recovery from membrane concentrates (depending on the concentrate composition). These technologies are ammonium recovery or struvite recovery either with electrodialysis combined with crystallization or with MAP crystallization and recovery of calcium phosphate either with EPR process or with combined process of electrodialysis and crystallization. Salt recovery from the membrane

concentrates of municipal wastewater was seen as a beneficial approach only in wastewater treatment plants where high salinity wastewater is treated. Advanced oxidation such as PCD oxidation could be applied to residual concentrate in order to increase the biodegradability of the concentrate and enable its recirculation to the biological degradation process. By applying these advanced concentrate treatment technologies, it could be possible to reach near-zero waste conditions in municipal wastewater treatment, providing that the recovered nutrients are utilized as fertilizers and the residual concentrate from nutrient recovery is recirculated back to the biological process. The final selection of different unit processes for concentrate treatment must be always done based on the concentrate origin (traditional or membrane based treatment before tertiary membrane process) and composition (potential presence of harmful impurities) so that the goals for the treatment can be met, while taking every safety aspect into account.

The implementation of these advanced concentrate treatment technologies in municipal wastewater treatment faces various challenges, mainly related to cost issues and legislation, which could hinder the adoption of these technologies on a full commercial scale. The current market situation and current legislation do not provide sufficient incentives or any requirements to implement novel technologies to the wastewater treatment, which could produce high quality effluents and simultaneously recover nutrients and reduce chemical use. However, the depletion of valuable raw materials such as phosphorus, as well as dangers associated with the potential presence of harmful impurities, such as organic micropollutants, microplastics and antibiotic resistant bacteria, in aqueous environments create a need for further research and stricter legislation. It is foreseen that in the future the membrane concentrates are more often seen as valuable raw material for resource recovery rather than a waste stream. In this context, new modern advanced membrane concentrate treatment technologies and processes pursuing towards optimal resource recycling whilst ensuring the process safety throughout the concentrate treatment are likely to be researched more and become more viable in the future, both economically and technologically.

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Publication II

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Novel process concept alternatives for improved removal of micropollutants in wastewater treatment

Novel process concept alternatives for improved removal of micropollutants in wastewater treatment

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ABSTRACT

Conventional activated sludge treatment plants have limited capability to remove micropollutants from municipal wastewater, and as a consequence, concentrations of micropollutants in water bodies are increasing. This creates concerns due to their potentially harmful effects on the aquatic environment, as well as needs to improve or replace the traditional wastewater treatment processes with novel process concepts. In this study, two novel process concept alternatives for enhanced removal of micropollutants are examined. The experiments were done in pilot scale with real wastewater of a small municipality. In the first concept, a membrane bioreactor process (MBR) without phosphorus precipitation was combined with high permeability nanofiltration (NF), and in the other, the MBR with the precipitation of phosphorus was combined with advanced oxidation implemented by pulsed corona discharge (PCD). The results showed that the MBR processes were insufficient for removing unreadily biodegradable micropollutants, such as carbamazepine and diclofenac. However, combining the nanofiltration or PCD oxidation step with the MBR enabled significant enhancement in the removal of micropollutants. Over 84% removal was reached with nanofiltration (NF270) for most of the studied micropollutants, except caffeine and hydrochlorothiazide. The performance of PCD oxidation (oxidation energy 0.2 kWh/m^3) in the removal of micropollutants exceeded the one of nanofiltration; over 90% removal of most of the studied micropollutants was reached, and the pollutants were degraded below 0.1 μg/L concentration. Thus, the total removal of micropollutants was better in the concept combining MBR and oxidation treatment. However, the concept combining MBR and nanofiltration provided better overall removal of organic compounds (removal of COD and DOC > 99%), and it also enabled the recovery of phosphorus as a concentrated solution.

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1. Introduction

The presence of micropollutants, such as pharmaceuticals and pesticides in aqueous environments is an increasing concern due to their potentially harmful effects on aquatic life. The occurrence of these micropollutants has recently become more evident due to improved analytical methods with lower detection limits [1–5]. Conventional activated sludge processes (CAS), which are nowadays typically used in the treatment of municipal wastewater, are not specifically designed for the removal of micropollutants [2,5].

Compared to CAS processes, membrane bioreactors (MBR) might be a more efficient process option for the removal of micropollutants from municipal wastewater, because higher sludge retention times (SRTs) are typically used in MBRs than in CAS processes. However, although a high SRT usually enhances the degradation of compounds having low biodegradability, it has been shown that efficient removal of all micropollutants will not be achieved by using the MBR process alone. For instance, several researchers have reported lower than 20% removal of micropollutants, such as carbamazepine and diclofenac, or very hydrophilic substances possessing strong electron-withdrawing functional groups, in the MBR process [3,6–8]. Better removal (70–90%) has been reported for hydrophilic antibiotics, such as sulfamethoxazole and sulfamethazine, by Sahar et al. [8].

The use of a reverse osmosis (RO) process as a post-treatment after MBR or CAS has been reported to be an efficient technology option for enhanced removal of micropollutants [6,8–12]. Dolar

et al. [6] report over 99% removal of challenging micropollutants such as carbamazepine, atenolol and sotalol with a negatively charged RO membrane (Ropur TR70-4021-HF) having a molar mass cut-off (MMCO) of 100 Da. In addition, it has been concluded in several studies that over 95% of various micropollutants, such as carbamazepine, diclofenac and atenolol can be removed from wastewater with RO membranes such as SW30 (DOW) and ESPA2 (Hydranautics) [8,13,14]. It has also been reported that the use of nanofiltration membranes can result in high removal rates of micropollutants. For example, Azaïs et al. [9] report retentions around 82 and 93% for atenolol and carbamazepine with an NF270 membrane in the filtration of a MBR effluent, whereas retentions around 95 and 98% were achieved with a tighter NF90 membrane.

In addition to membrane filtration processes, also several advanced oxidation processes (AOPs), such as ozonation, O_3/H_2O_2, fenton, photo-fenton, solar photo-fenton, photocatalytic oxidation, and pulsed corona discharge (PCD) have been studied as advanced micropollutant treatment options after a MBR or CAS process [4,15–18]. The efficiency of AOPs is based on strong oxidants, mainly hydroxyl radicals (·OH) and ozone (O_3), which are able to degrade organic compounds such as micropollutants [19]. In these processes, oxidation occurs through direct reactions with molecular ozone, as well as indirect reactions with ·OH radicals produced by ozone decomposition [20]. Direct reactions with ozone are slow compared to ·OH radicals, and the degradation of organic compounds by ozone is efficient for target substances, such as many micropollutants like diclofenac and carbamazepine, which have high electron-density functional groups as in double bonds, activated aromatic systems or amino groups [20,21]. Thus, AOPs are often based on the enhanced formation of ·OH radicals, which react very fast and non-selectively with almost any dissolved organic compound and the water matrix [19–22]. The efficiency of advanced oxidation in micropollutant degradation is dependent on the feed matrix due to the non-selective nature of ·OH radicals, as they can be scavenged by the dissolved organic matter (DOM) and the carbonates/bicarbonates present in the feed water [19].

According to Reungoat et al. [16], high removal rates of >98, >94, >93 and 77% for carbamazepine, diclofenac, trimethoprim and atenolol, respectively, could be reached with direct ozonation of the CAS secondary effluent (11 mg/L dissolved organic carbon, DOC) by the ozone dose of 0.5 mg O_3/mg DOC. O_3/H_2O_2 oxidation of the CAS secondary effluent (TOC 7 mg/L) with ozone to the total organic carbon (O_3:TOC) ratio of 0.8 (ozone dose 5 mg/L) and H_2O_2 addition at a H_2O_2/O_3 molar ratio of 1.0 (dose 3.5 mg/L) reached high removal rates for carbamazepine (>99%), diclofenac (>99%), trimethoprim (>99%) and atenolol (>99%) according to Gerrity et al. [18]. Dobrin et al. [17] reached over 99% removal of diclofenac (degradation below detection limit) from a model solution (50 mg/L diclofenac in tap water) with 15 min PCD treatment.

As discussed above, both RO and oxidation processes have been shown to be capable of efficient removal of micropollutants, but the operational costs are often relatively high, either due to high energy consumption (total energy consumption > 1.5 kWh/m³) or high chemical consumption (pH adjustment, reagent, precipitation etc.) [4,9,15,23]. The costs can be decreased by replacing RO with NF. For instance, higher than 55,000 $ annual cost savings could be reached in the water reclamation process (425 m³/h) when RO membranes (ESPA2) were replaced by high permeability nanofiltration membranes (NF270) [23]. Regarding AOPs, PCD oxidation can be over two times more energy-efficient than traditional ozonation [4].

As shown above, the process concepts utilizing membrane filtration (NF or RO) or AOPs after an MBR or CAS process seem to be efficient for the removal of micropollutants. In this study, two novel process concepts for enhanced removal of micropollutants,

mainly pharmaceuticals, from municipal wastewater are compared. In the studied concepts, MBR treatment operated without chemical precipitation of phosphorus, and traditional MBR treatment in which phosphorus was precipitated were used as the main treatment, and nanofiltration or PCD oxidation as a tertiary treatment. The selection of the unit operations was based on the aim to develop a cost-efficient process, which would enable the removal of 90% of the studied micropollutants and also maintain acceptable removal of organic compounds and nutrients in order to inhibit the eutrophication effect of the discharge waters.

2. Materials and methods

The studied process concepts are illustrated in Fig. 1. In concept A the chemical consumption is reduced compared to the traditional MBR treatment, because MBR was operated without chemical precipitation of phosphorus. In this concept, the enhanced removal of micropollutants and organic compounds was done by applying high permeability nanofiltration (NF) as the tertiary treatment. This enabled the recovery of phosphorus from the NF concentrate, which means that the recovered phosphorus could be in a more readily usable form, as it is not tightly bound with iron salts, such as the phosphorus recovered in the traditional MBR process (process concept B). In the evaluated process concept B, the PCD treatment was used for further purification of the wastewater after the traditional MBR (with precipitation) process.

2.1. MBR and NF pilot processes

An MBR pilot unit (Alfa Laval) containing two separate process lines (MBR without chemical precipitation of phosphorus (process concept A) and MBR with chemical precipitation of phosphorus (process concept B)) was operated in parallel with a full-scale conventional activated sludge process (CAS) in a small municipality in Finland. In the MBR pilot, MFP2 microfiltration membranes made from polyvinylidene fluoride (PVDF) (pore size 0.2 µm, average permeability > 500 L/(m²h bar), and contact angle around 80°) were used [24, data from the manufacturer]. In concept B, the removal of phosphorus was done by adding 300 mg/L of ferric sulfate to the denitrification stage (PIX-105, Kemira Oyj). The CAS process was a traditional activated sludge plant including a primary screen, a sand removal unit, an activated sludge stage, and a clarifier (no pre-clarifier), followed by tertiary sand filtration (Dynasand filters). The process parameters used in the MBR and CAS processes are presented in Table 1.

A 2.5″ nanofiltration spiral wound module containing the NF270 membrane from DOW was used in the NF process to treat the MBR permeate (Fig. 1) in process concept A. The NF270 membrane has a cross-linked semi-aromatic polyamide active layer on a polysulfone support. The molar mass cut-off (MMCO) value of the NF270 membrane is 220–250 Da, and the contact angle is 30°. The NF270 membrane is negatively charged in the neutral pH area [9,25,26]. During the research period reported here, the average flux in the NF process was 22 L/(m²h) (13–31), the filtration temperature 14 °C (9–17), the transmembrane pressure (TMP) 5.4 bar (2–12), and the recovery rate 84% (68–92).

2.2. PCD oxidation

In process concept B, the non-thermal plasma advanced oxidation method in the form of gas-phase pulsed corona discharge (PCD) was used to degrade the micropollutants in the permeate of the MBR, applied with the precipitation of phosphorus. The degradation of micropollutants took place in a PCD reactor, where ozone and ·OH radicals are generated from oxygen and water by
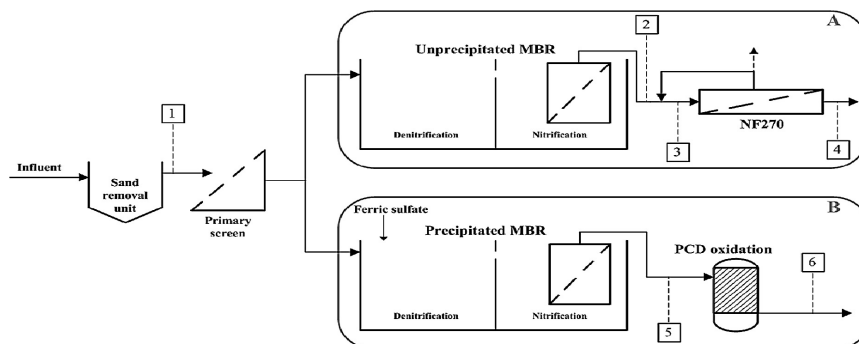
Fig. 1. Studied process concepts (A and B) for enhanced micropollutant removal from municipal wastewater. The sampling points for micropollutant research are marked with numbers 1–6. The 7th sampling point was treated effluent from the CAS process.

Table 1
Process parameters in the studied biological processes. The presented values are average values during a micropollutant research period (n = 3,) and the range is given in brackets, if applicable. The average dose of ferric sulfate was 300 mg/L. The MBR processes were operated at a constant flux mode, and aeration was kept constant.

Parameter	CAS	MBR, concept A	MBR, concept B
Flux, L/(m^2 h)	–	10	10
Mixed liquor suspended solids (MLSS), g/L	6	10 (8.6–11.1)	10 (7.6–11.1)
MBR aeration, Nm^3/h	–	6	6
pH in aeration	>6.5	6.8 (6.5–7)	6.8 (6.5–7)
Temperature in aeration, °C	8 (6–9)	10 (8–13)	10 (8–13)
Dissolved oxygen (DO), mg/L	>2	2.5 (2–3)	2.5 (2–3)
Sludge retention time (SRT), d	81 (79–83)	48 (33–57)	33 (24–39)
Hydraulic retention time (HRT), h	70 (67–74)	21	21

using small energy input from a pulse generator [4,27]. Oxidation reactions for the degradation of contaminants, as well as a further description of the PCD equipment used in this study have been described by Panorel et al. [27]. More detailed description of the PCD equipment used have been also presented in the supplementary material (S1).

The operational parameters used in the PCD oxidation were the pulse repetition frequency (840 pulses per second), atmosphere composition (91% oxygen) and oxidation energy (0.2 kWh/m^3). Oxygen was introduced to the reactor before the oxidation experiment to achieve an average oxygen concentration of 91% during oxidation. The experiment was performed at room temperature. A 50 L sample of MBR permeate was used in the oxidation experiment. The recirculation flow rate in the PCD reactor was around 15 L/min. The pH of the permeate was 6.3, conductivity 603 μS/cm, dissolved organic carbon (DOC) 8 mg/L, chemical oxygen demand (COD) 16 mg/L, biochemical oxygen demand (BOD) <2 mg/L, and specific UV absorbance (SUVA$_{254nm}$) 1.6 L/mg m.

2.3. Micropollutants, sampling and analytical procedures

17 different micropollutants (Table 2) including 16 pharmaceuticals and one pesticide, were identified from the samples. The sampling was implemented three times during an eight-week period at the end of the piloting experiments, which took eight months in total. The samples for micropollutant analysis were taken from seven different sampling points (Fig. 1):

(1) Influent (CAS/MBR)
(2) MBR permeate (concept A)

(3) NF270 concentrate (concept A)
(4) NF270 permeate (concept A)
(5) MBR permeate (concept B)
(6) PCD effluent (concept B)
(7) CAS effluent.

The samples were collected in glass bottles of 1L and kept at 4 °C after sampling before analysis. The analysis was started within 24 h of sampling. The sampling of the influent was executed with an automatic 24 h sampler. The sampling for other samples was carried out within one day as a collection sample from five partial samples taken at different times of the day in order to ensure the representativeness of the samples. The samples of PCD oxidation were taken as single samples from a laboratory batch experiment. The pharmaceuticals were determined by using solid phase extraction as a pretreatment, and ultra-performance liquid chromatography coupled with mass spectroscopy analysis (UPLC/MS/MS) for micropollutant identification. The analysis method was based on the standards EPA 1694 and EPA 539 (modified). The pesticide N, N-diethyl-meta-toluamide (DEET) was determined by using solid phase extraction as pretreatment and by gas chromatography coupled with mass spectroscopy analysis (GC/MS/MS). The limit of detection (LD) for the pharmaceuticals and pesticide were between 0.001 and 0.5 μg/L, depending on the sample matrix and the micropollutant to be analyzed. The specific limit of detection for each micropollutant in different sample matrices has been presented in the supplementary material S2 (Table S1). [28]

Table 2 presents also the acid dissociation constants pKa, which describe the acidity of a specific molecule. If the pKa value of a pollutant is lower than the pH of the wastewater or sludge, it is con-

Table 2
Molecular characteristics of the studied micropollutants and average micropollutant concentrations in the influent for the CAS and MBR process.

Micropollutant	Classification	Formula	Molar mass, g/mol	pKa, –	log K_{ow}, –	K_d, L/kg$_{SS}$	K_{biol}, L/g$_{SS}$/d	Influent concentration, µg/L
DEET (N,N-diethyl-meta-toluamide)	Pesticide, insect repellent	$C_{12}H_{17}NO$	191.3 [34]	<2 [35]	2.0 [34]	–	–	0.34 ± 0.19
Paracetamol	Pain killer	$C_8H_9NO_2$	151.2 [34]	9.4 [34]	0.46 [34]	0.4 [33]	106–240 [33]	44.5 (19–68)
Ibuprofen	Pain killer	$C_{13}H_{18}O_2$	206.3 [34]	4.9 [34]	4.0 [34]	7 ± 2 [33]	9–22 [33]	16 ± 4
Ketoprofen	Pain killer	$C_{16}H_{14}O_3$	254.3 [34]	4.5 [34]	3.1 [34]	72 ± 111 [36]	–	0.98 (0.48–2.0)
Diclofenac	Non-steroidal anti-inflammatory drug	$C_{14}H_{11}Cl_2NO_2$	296.2 [34]	4.2 [34]	4.5 [34]	16 ± 3 [31,33,37]	≪0.1 [31,33,37]	1.85 (1.40–2.70)
Naproxen	Non-steroidal anti-inflammatory drug	$C_{14}H_{14}O_3$	230.3 [34]	4.2 [34]	3.2 [34]	10–13 [33,37]	0.4–0.8 [33]	3.3 (2.0–5.9)
Carbamazepine	Anti-epileptic agent and mood stabilizer	$C_{15}H_{12}N_2O$	236.3 [34]	13.9 [34]	2.5 [34]	1.2 [3,37]	<0.01 [37]	0.45 ± 0.05
Citalopram	Antidepressant and drug for alcoholism	$C_{20}H_{21}FN_2O$	324.4 [34]	9.59 [38]	3.5 [34]	–	–	0.31 (0.22–0.46)
Atenolol	Cardioselective beta blocker	$C_{14}H_{22}N_2O_3$	266.3 [34]	9.6 [34,39]	0.16 [34,39]	5.9 ± 4.4 [36]	[a]0.69 [39]	0.49 (0.45–0.57)
Bisoprolol	Cardioselective beta blocker	$C_{18}H_{31}NO_4$	325.4 [34]	9.4 [40]	1.9 [34]	–	–	1.19 ± 0.25
Metoprolol	Selective beta blocker	$C_{15}H_{25}NO_3$	267.4 [34]	9.7 [39]	1.9 [34,39]	[b]1 [39]	[a]0.58 [39]	1.9 (1.5–2.2)
Sotalol	Beta blocker, Beta-antagonist	$C_{12}H_{20}N_2O_3S$	272.4 [34]	8.4 [41]	0.24 [34]	[b]37 [39]	[a]0.29 [39]	1.0 (0.33–2.80)
Furosemide	Loop diuretic	$C_{12}H_{11}ClN_2O_5S$	330.7[34]	3.8 [34]	2.0 [34]	140–160 [42] (Log K_d 2.15–2.2)	–	14.2 (8.0–32.0)
Hydrochloro-thiazide	Thiazide diuretic	$C_7H_8ClN_3O_4S_2$	297.7 [34]	7.9 [34]	−0.07 [34]	23.5 ± 12.6 [36]	–	11.3 (6.1–18.0)
Trimethoprim	Antibiotic, Dihydrofolate reductase inhibitor antibacterial	$C_{14}H_{18}N_4O_3$	290.3 [34]	7.1 [34]	0.91 [34]	225–330 [36,37,43]	0.05–0.22 [36,37,43]	0.58 (0.48–0.65)
Tetracycline	Antibiotic, Tetracycline-class antimicrobial	$C_{22}H_{24}N_2O_8$	444.4 [34]	3.3 [34]	−1.4 [34]	–	–	6.2 (1.2–16.0)
Caffeine	Stimulant for central nervous system	$C_8H_{10}N_4O_2$	194.2 [34]	14.0 [34]	−0.07 [34]	–	–	107 (26–160)

Data obtained from [3,31,33–43].
[a] Unit for K_{biol} of atenolol, metoprolol and sotalol is L/g$_{COD}$/d.
[b] Unit for K_d of metoprolol and sotalol is L/kg$_{COD}$.

sidered to be dissociated and charged [12,29]. Log K_{ow} describes the hydrophobicity/hydrophilicity of a substance. If the log K_{ow} value is higher than 3.2, the substance is considered to be clearly hydrophobic and have a higher tendency to be absorbed into particles in wastewater [7,12,30]. The sorption of substances to the sludge via adsorption can be estimated by the K_d value, which is the ratio of the concentration of the substance between the solid and aqueous phase at equilibrium conditions [3,31]. A K_d value of 500 L/kg$_{SS}$ is considered to be a limit value for significant removal by sorption [3,32]. The tendency of a substance for biological degradation can be estimated by the degradation constant K_{biol}. The biological degradability of compounds can be classified in the following way [3,33]:

K_{biol} < 0.1 L/g$_{SS}$/d: limited removal by degradation (<20%)
0.1 < K_{biol} < 10 L/g$_{SS}$/d: partial removal by degradation (20–90%)
K_{biol} > 10 L/g$_{SS}$/d: efficient removal by biological degradation (>90%)

The dissolved organic carbon (DOC) of the samples was analyzed with a Shimadzu TOC-L total organic carbon analyzer. For DOC analysis, the samples were centrifuged (10 min, 3500 rpm) with an ELMI CM-6MT centrifuge. In addition, the samples taken from the PCD oxidation were analyzed also by prefiltration with 0.45 µm Nylon filters as the pretreatment method. These values were used to determine the SUVA values of the samples taken from the PCD oxidation process. The UV absorbances for the SUVA analyses were measured with a JASCO V-670 UV–Vis-

spectrophotometer at 254 nm (the samples were prefiltered with the 0.45 µm Nylon filter). The SUVA value is a parameter describing the amount of aromatic substances in the sample, and a potential decrease in the SUVA values during PCD oxidation is an indication of the degradation of aromatic micropollutants. The COD analyses (total COD) were made with a Hach DR2010 spectrophotometer at 420 nm (COD LR, DIN ISO 15705). The total nitrogen (determination limit 200 µg/L) and phosphorus (determination limit 2 µg/L) were analyzed at a Finas accredited environmental laboratory (T032, SFS-EN ISO/IEC 17025:2005). Total nitrogen analysis (SFS-EN ISO 13395 (1997) FIASTAR AN 5202/2000) had an error margin of 20–50% at lower concentrations (200–358 µg/L) and 10–20% error margin at concentrations above 358 µg/L. Total phosphorus analysis (inoperative standard SFS-3026 (1986)) had an error margins of 20–50% (concentrations 2.0–7.5 µg/L) and 10–20% (>7.5 µg/L).

The removal efficiencies of the biological processes and the oxidation process are presented as percentage removal rates (Eq. (1)). Eq. (1) was also used to calculate the retention in the NF stage by replacing the $C_{i\ influent}$ and $C_{i\ effluent}$ values with the NF feed and permeate values at a recovery of 84%.

$$\text{Removal rate} = (1 - (C_{i\ effluent}/C_{i\ influent})) \times 100\% \tag{1}$$

where $C_{i\ effluent}$ is the concentration of substance (i) in the effluent (after biological or oxidation process) and $C_{i\ influent}$ is the concentration of substance (i) in the influent

Table 3

Removal of biodegradable pharmaceuticals in CAS and studied process concepts A and B (n = 3). Presented removal rates are average values (n = 3), range given in brackets if applicable. Oxidation energy in PCD 0.2 kWh/m^3 (single experiment). The average flux in NF270 process 22 L/m^2 h and the recovery rate 84%.

Micropollutant	CAS, %	Concept A		Concept B	
		MBR, %	NF270, %	MBR, %	PCD, %
Paracetamol	>97	>99	>97	>99	>90
Ibuprofen	>99	>99	>96	98.5 (96.4–99.7)	>90
Ketoprofen	75.7 (75–76.3)	90.1 (88.5–92.1)	>88	81.3 (77.1–83.8)	81.5
Naproxen	>95	>97	96.3 (95.5–97.1)	90.2 (86.5–94.1)	>94
Caffeine	99.8 (99.6–99.9)	99.7 (99.6–99.8)	75.8 (52.0–95.0)	99.5 (99.1–99.8)	90.8
Tetracycline	>97	>95	>90	>95	–

3. Results and discussion

3.1. Removal of pharmaceuticals and DEET

Six pharmaceuticals of the studied 16 (paracetamol, ibuprofen, ketoprofen, naproxen, caffeine and tetracycline) were removed from the wastewater efficiently already in the biological MBR and CAS processes (Table 3, Table S2). This could be expected, because these substances, especially pain killers as well as caffeine, are readily biodegradable [33,43,44–46] (Table 2). In addition, the sorption of micropollutants to sludge is another important removal mechanism for certain micropollutants, as Kim et al. [47] suggests for tetracycline. The concentration of target micropollutants in the CAS influent and after each treatment process studied in this work has been presented in the supplementary material S3 (Tables S2–S4).

Nanofiltration enabled decreasing the amount of most of the biodegradable pharmaceuticals, except caffeine, in the biologically treated wastewater. The relatively hydrophobic nature of ibuprofen, ketoprofen and naproxen (Table 2) could enhance their removal in nanofiltration. The low removal efficiency of caffeine in the NF step might originate from the small size, hydrophilicity and uncharged nature of caffeine (Table 2). Improved removal of these pharmaceuticals, including caffeine, could be achieved also when the MBR process was combined with PCD oxidation (Table 3).

The removal of beta blockers (atenolol, bisoprolol, metoprolol and sotalol) was shown to be limited in the CAS process and the MBR processes (Table 4, Table S3). According to Maurer et al. [39], the major removal mechanism for atenolol and sotalol in CAS and MBR processes is biodegradation. However, the degradation rates were low, as the K_{biol} values (Table 2) show, and thus degradation was often incomplete [39]. The highest removal efficiency (around 70%) was achieved for atenolol in the MBR processes. The removal of the other beta blockers was modest, typically below 40%. The average removal rates of 71% (concept A) and 69% (concept B) for atenolol observed in this study with the studied MBR processes (HRT about 21 h) (Tables 1 and 4) were very similar to the average removal rate of 77% for atenolol

reported by Radjenovic et al. [36] in an MBR process operated at a HRT value of 15 h.

As shown in Table 4 and Table S3, the removal of diuretics (furosemide and hydrochlorothiazide) in the biological processes was modest in this study, the removal rates being below 50%. These diuretics, especially hydrochlorothiazide, are hydrophilic (Table 2), and based on the results observed in this study and the results of Radjenovic et al. [36], they can be expected to be poorly biodegradable. Furosemide has also a low pKa value of 3.8 (Table 2), and thus removal due to bounding into particles can be expected to be limited. Urtiaga et al. [48] also report a modest removal of furosemide, i.e. 25 and 17% in CAS and tertiary UF processes.

The biological processes removed less than 30% of mood drugs and the anti-inflammatory drug diclofenac and less than 60% of the antibiotic trimethoprim (Table 5, Table S4). The major reason for the modest removal of these pharmaceuticals is their low biodegradability. Especially carbamazepine and diclofenac have very low biological degradation constants (K_{biol} < 0.1 L/g_{SS}/d) (Table 2). Negligible or no removal of these pharmaceuticals in MBR and CAS processes has been observed earlier by Li et al. [3], Tadkaew et al. [7], Sahar et al. [8], Miao et al. [49], and Vieno et al. [50]. The results of the MBR experiments (Table 5) showed that carbamazepine concentration in the effluent was even higher than in the influent. This has been noted also by Li et al. [3] and Vieno et al. [50]. According to Vieno et al. [50], this could be explained by the fact that the amount of carbamazepine increases due to enzymatic conversion of carbamazepine metabolites in the influent to the parent compound during the MBR process. Similar phenomena may also explain the negative removal percentage observed for other pollutants (Table 4 and 5) in this study.

Both of the studied MBR processes removed DEET (N,N-diethyl-meta-toluamide) better (average removal 94%) than the CAS process (average removal 72%, Table 5). This was not expected, based on Bernhard et al. [51] who report that the removal of DEET is dependent on the SRT value, and a higher SRT value enhances removal. In this study the SRT value in the CAS process was higher than in the MBR processes (Table 1). The higher DEET removal in the MBR processes could thus in this case be at least partly explained by molecule-membrane interactions, since the

Table 4

Removal rate of beta blockers and diuretics in CAS and in MBRs, as well as NF and PCD processes n = 3). The presented values are average removal rates, and the range is given in brackets, if applicable. Oxidation energy in PCD 0.2 kWh/m^3 (single experiment). The average flux in the NF270 process 22 L/m^2 h and the recovery rate 84%. The MBR process in concept A was operated without phosphorus precipitation.

Micropollutant	CAS, %	Concept A		Concept B	
		MBR, %	NF270, %	MBR, %	PCD, %
Atenolol	3.3 (−27 to 33)	70.8 (56–86)	87.4 (82–94)	69.1 (64–74)	>95.5
Bisoprolol	4.8 (−7.7 to 15)	41.9 (0–65)	90.6 (83–96)	21.7 (0–36)	99.0
Metoprolol	19.4 (6.7–33)	18.8 (−6.7 to 58.6)	84.3 (72–97)	20.1 (0–32)	98.5
Sotalol	−37.5 (−42 to −33)	−27.7 (−42 to −13)	84.4 (79–92)	−33.0 (−33.3 to −32.6)	>98.1
Furosemide	46.5 (33–73)	16.3 (0–38)	95.2 (90–99)	5.6 (−10 to 34)	>99.2
Hydrochlorothiazide	−22.8 (−57 to 25)	27.5 (−21 to 74)	54.7 (50–59)	2.4 (−43 to 34)	>98.7

Table 5
Removal of diclofenac, carbamazepine, citalopram, trimethoprim and DEET in CAS and the studied process concepts A and B (n = 3). The presented values are average removal rates and the range is given in brackets, if applicable. Oxidation energy in PCD 0.2 kWh/m³ (single experiment). The average flux in NF270 process 22 L/m² h and the recovery rate 84%. The MBR process in concept A was operated without phosphorus precipitation.

Micropollutant	CAS, %	Concept A		Concept B	
		MBR, %	NF270, %	MBR, %	PCD, %
Diclofenac	19.1 (−41 to 74)	11.7 (−36 to 53)	97.4 (96–98)	−24.6 (−47 to −13)	>96.1
Carbamazepine	−32.9 (−54 to −12)	−36.4 (−48 to −24)	87.6 (81–95)	−29.8 (−34 to −26)	>99.1
Citalopram	27.3 (4.5–47)	24.9 (15–32)	96.6 (95–98)	22.2 (4.5–33)	>94.1
Trimethoprim	58.4 (51–73)	8.2 (6.2–10)	88.9 (81–97)	−11.1 (−20 to −3)	>99.8
DEET (N,N-diethyl-meta-toluamide)	71.8 (57–88)	94.4 (92–98)	>88.3 (80–95)	93.5 (91–96)	>66.7

membrane used in the MBR pilot and DEET have corresponding hydrophobicity (membrane contact angle 80°, DEET Log K_{ow} value 2), and thus adsorption of DEET into the membrane structure could be possible. The advanced treatment methods NF (concept A) or PCD (concept B) used after the MBR treatment enhanced the removal of DEET further and decreased the concentration below detection limits (0.005 µg/L).

Nanofiltration with the NF270 membrane removed efficiently the beta blockers and diuretics, (except hydrochlorothiazide) left in the wastewater after the MBR treatment (Fig. 1 and Table 4). The retentions were higher than 84%. The size of the beta blockers under examination were higher compared to the cut-off value of the NF270 membrane (220–250 Da), which indicates that size exclusion is one of their separation mechanisms ([9], Table 2). The difference in the average removal rates between furosemide (95%) and hydrochlorothiazide (55%) (Table 4) would indicate that also other removal mechanisms had an effect on the removal of diuretics. As presented in Table 2, the molar masses of the diuretics are close to each other, and from this point of view, their retentions based on size exclusion could be expected to be similar. However, a difference in their retentions was observed, and this can be explained by the higher hydrophobicity and charged nature of furosemide (log K_{ow} 2.0 and pKa 3.8) compared to hydrochlorothiazide (log K_{ow} −0.07 and pKa 7.9).

Nanofiltration with the NF270 membrane removed efficiently also the mood drugs (citalopram and carbamazepine), as well as diclofenac and trimethoprim, the average retentions being higher than 87%. Size exclusion was presumably the major separation mechanism for these micropollutants, since these pollutants, except carbamazepine, have higher molar mass than the nominal cut-off value of the NF270 membrane. Moreover, the relatively hydrophobic nature of diclofenac, citalopram and carbamazepine (Table 2) could also enhance their separation. The 88% average retention for carbamazepine measured in this study was slightly lower than the retentions 93 and 92% reported by Azaïs et al. [9] and Gur-Reznik et al. [14] with the NF270 membrane in the filtration of an MBR permeate.

The treated MBR permeate from the precipitated MBR process was virtually solid-free, and the concentration of organic impurities was small (see Table 1). Thus, only a small fraction of the ·OH radicals created in the PCD treatment was scavenged by the water matrix, which resulted in a high degradation efficiency even with the relatively low energy dose used in oxidation (0.2 kWh/m³). PCD oxidation removed also efficiently the studied beta blockers and diuretics which were left in the wastewater after the MBR treatment (Table 4). For instance, the concentrations of atenolol and sotalol were below detection limits (<0.01 µg/L) after the PCD treatment. PCD oxidation decreased also the concentration of mood drugs, diclofenac and carbamazepine, significantly, the concentrations being below 0.05 µg/L for all these pollutants after oxidation.

PCD oxidation degraded also diclofenac and trimethoprim very efficiently (Table 5), which were only partially removed in biolog-ical treatment. Reungoat et al. [16] and Dobrin et al. [17] report similar results about the removal of diclofenac with AOP treatment. Reungoat et al. [16] report over 94 and 77% removal for diclofenac and trimethoprim, respectively, with direct ozonation (0.5 mg O₃/mg DOC). Dobrin et al. [17] reached over 99% removal of diclofenac with a 15 min PCD treatment of a model solution (50 mg/L diclofenac in tap water). Energy consumption of 59.2 kWh/m³ (energy yield of 0.76 g/kWh for 90% conversion) was needed for oxidation [17]. It can be concluded that in this study, the PCD treatment decreased the concentrations of all the 17 micropollutants studied to below 0.1 µg/L, even at a low oxidation energy of 0.2 kWh/m³.

3.2. Comparison of the studied process concepts

The studied process concepts A and B (Fig. 1) differed from each other in the operation of the MBR processes (without precipitation and with precipitation), and in the applied tertiary treatment step (nanofiltration or PCD oxidation). Comparison of the studied concepts was made on the basis of treatment efficiency related to the removal of micropollutants, organic compounds and nutrients (Table 6). Moreover, energy consumption, as well as chemical consumption in the MBR process were taken into account. Investment costs were not included, because their evaluation is challenging due to insufficient investment cost data available for PCD oxidation. In addition, maintenance costs related to replacing of process equipment etc., as well as membrane cleaning costs were excluded.

The removal of micropollutants under examination was slightly better in the MBR process where precipitation was not applied (concept A), compared to the MBR process with precipitation (concept B) (Table 6). This was presumably mainly due to the higher SRT of 48 days in the MBR process without precipitation (33 days in the MBR with precipitation). Long sludge and hydraulic retention times in MBR processes have been reported to enhance the removal of micropollutants via biodegradation [2,8,52,53]. However, the concentrations of many of the unreadily biodegradable micropollutants, such as diclofenac and carbamazepine, were still rather high after the MBR treatments.

Both tertiary treatments applied here, nanofiltration (concept A) and PCD oxidation (concept B) removed the studied micropollutants from the MBR permeates efficiently. However, in nanofiltration the removal of some substances, such as caffeine and hydrochlorothiazide, was limited, for which an average removal of 76 and 55% was obtained. This corresponded to average concentrations of 0.22 and 7.83 µg/L in the NF permeate. The somewhat limited removal of these pollutants may have been due to their small size or hydrophilicity. PCD oxidation gave better performance by degrading all micropollutants below the residual concentration of 0.1 µg/L. The hydroxyl radicals generated in PCD treatment are especially efficient in the degradation of aromatic structures [4,27]. Most of the analyzed micropollutants were aromatic compounds, and thus the PCD oxidation process degraded

Table 6
Overall removal efficiencies of COD, DOC, P_{tot} and N_{tot}, as well as selected micropollutant groups in the studied process concepts. The presented values are average values during the micropollutant research period (n = 3), or the overall removal range is given (micropollutants). The average dose of ferric sulfate in the MBR process (concept B) 300 mg/L. Oxidation energy in PCD 0.2 kWh/m³. The average flux in NF270 process 22 L/m² h and the recovery rate 84%.

Removal efficiency, %	CAS	Concept A			Concept B		
		MBR	NF270	Total	MBR	PCD	Total
COD	87	91	99	>99	92	0 ± 20	92
DOC	–	82	97	>99	86	0	86
P_{tot}	93	55	96	98	99	–	99
N_{tot}	24	60	11	64	40	–	40
Painkillers	81–>98	>90–>99	>89	>99	81–>99	82–>90	>96
Beta blockers	−38 to 19	−28 to 71	84–91	>79	−33 to 69	>95–99	>93
Diclofenac	19	12	97	>97	−25	>96	>95
Carbamazepine	−33	−36	88	>83	−30	>99	>98

them very efficiently. The degradation of aromatic structures in oxidation was also noticed as a 27% decrease in the SUVA value.

As regards the removal of organic compounds and nutrients, both of the studied concepts exceeded the efficiency of the CAS process (Table 6). In concept A, more organic compounds (other than micropollutants) were removed than in concept B. The PCD treatment used in concept B removed only small amounts of organic compounds measured as COD and DOC, although the results showed clearly that the amount of micropollutants decreased due to oxidation. This can be explained by the very small amounts of micropollutants: a significant change in their amounts could not be detected as a significant decrease of COD and DOC values within the measurement accuracy. Due to the small decrease in COD and DOC, significant mineralization was not reached with the used oxidation parameters. This indicates that oxidation by-products were formed during the oxidation.

One of the most significant differences between the studied concepts was their capability to remove nitrogen. Concept A removed 60% of nitrogen, while concept B removed 40%. The higher SRT value in the MBR without precipitation probably enhanced the removal of nitrogen. The removal of phosphorus was as efficient in both studied concepts; the amount of phosphorus was about 0.1 mg/L in the treated water. However, in concept B this required a 300 mg/L dose of ferric sulfate, and phosphorus was precipitated into the MBR sludge. Thus, one advantage of the unprecipitated MBR compared to the precipitated MBR would be the potential cost savings in the use of precipitation chemicals. For instance, avoiding of the use of ferric sulfate (300 mg/L) for the precipitation of phosphorus would mean cost savings around 0.045 €/m³ [54]. In concept A, no chemical addition was needed, and phosphorus could be recovered from the NF concentrate for instance with an electrochemical phosphorus recovery process or crystallization [55–57]. In PCD oxidation (concept B), inorganics, such as phosphorus were not removed.

In this study, PCD oxidation used 0.2 kWh/m³ of oxidation energy in the degradation of micropollutants. The additional energy, which was required to produce oxygen to the PCD process, was estimated to be minor, since the feed effluent (MBR permeate) was well aerated and thus contained already significant amount of dissolved oxygen. Overall maximum consumption of oxygen during the PCD oxidation, including dissolution, was estimated to be between 30 and 40 g/m³, which would result to the cost of oxygen below 1 $cnt/m³ with the bulk oxygen [58]. The energy consumption of nanofiltration by using the NF270 membrane (in concept A) could be estimated to be in a similar range as the 0.87 kWh/m³ in the estimation of Bellona et al. [23] in a water reclamation process using the NF270 membrane (425 m³/h). This was because the NF270 spiral was in this study operated in similar conditions (flux 22 L/m² h and 84% recovery rate, TMP 5.4 bar) as in the study of Bellona et al. [23] (flux 26 L/m² h and 85% recovery, TMP 5.5 bar). By using an electricity price of 0.15 $/kWh [23], the cost savings

related to energy could be around 0.09 $/m³ when using PCD instead of nanofiltration with the NF270 membrane. Thus, process concept B utilizing PCD oxidation seems to be a promising approach for enhanced micropollutant removal according to this preliminary comparison study (Table 4). However, the exact content and harmfulness of the oxidation by-products formed in the PCD oxidation needs to be confirmed, and if there is a need for enhanced removal of organic compounds or even for the recovery of phosphorus, process concept A, combining the MBR without precipitation and high permeability nanofiltration could be more feasible.

4. Conclusions

In this study, two novel process concepts were compared for enhanced micropollutant removal:

(A) an MBR process without precipitation of phosphorus combined with high permeability nanofiltration (NF270), and
(B) an MBR process with precipitation combined with oxidation by using pulsed corona discharge.

Precipitation with ferric sulfate in the MBR process was not seen to have a beneficial effect on the removal of micropollutants or nitrogen. Limited removal of unreadily biodegradable micropollutants was noted in both MBR processes. Over 84% removal was reached with nanofiltration (NF270) for all the studied pollutants, except caffeine and hydrochlorothiazide. The performance of PCD oxidation (oxidation energy 0.2 kWh/m³) in the removal of micropollutants exceeded the one of nanofiltration; over 90% removal of most of the studied micropollutants was reached, and the micropollutants were degraded below a concentration of 0.1 µg/L. In general, better removal of micropollutants was achieved in concept B due to the high efficiency of PCD oxidation. However, the total removal of organic compounds was better in process concept A, where NF was used to polish the MBR permeate. Over 98% removal of phosphorus was noted in both tested concepts. Moreover, the use of concept A enabled the recovery of phosphorus from the nanofiltration concentrate.

This study presented an approach for future enhanced wastewater treatment processes, as both of the studied process concepts improved the effluent purity significantly. Process concept B, a combination of MBR with the precipitation of phosphorus and PCD oxidation, could be a feasible method for efficient micropollutant removal from real wastewater. However, the harmfulness of oxidation by-products needs to be confirmed before applying PCD oxidation in a full scale. Process concept A, MBR without chemical precipitation of phosphorus combined with NF, is a potential alternative for future sustainable wastewater treatment, especially when very efficient removal of total organic compounds

and nutrients is desired. This alternative enables also a decrease in chemical consumption, as well as the recovery of phosphorus as a concentrated solution.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.06.019.

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Publication III

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Two-stage nanofiltration for purification of membrane bioreactor treated municipal wastewater - minimization of concentrate volume and simultaneous recovery of phosphorus

Two-stage nanofiltration for purification of membrane bioreactor treated municipal wastewater - minimization of concentrate volume and simultaneous recovery of phosphorus

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ABSTRACT

This study evaluates the usability of a novel two-stage tertiary nanofiltration process concept for further purification of membrane bioreactor (MBR) permeate from municipal wastewater treatment and minimization of nanofiltration concentrate volume. In addition to water purification, the studied process aims to recover phosphorus from the second stage. The process concept for tertiary wastewater treatment includes two nanofiltration modules in series, where first stage is a nanofiltration of MBR permeate with a spiral-wound element and in the second stage a minimization of the NF concentrate is done by shear-enhanced nanofiltration combined with spontaneous precipitation and removal of precipitates from the concentration process. A volume reduction factor (VRF) of 300 was achieved with the studied process concept. The average permeabilities of the NF270 membranes used in both stages were 4.3 L/(m^{2}hbar) (first stage, spiral wound module) and 8.9 L/(m^{2}hbar) (second stage, high shear rate module). The two-stage NF process efficiently decreased the chemical oxygen demand (COD) and total organic carbon (TOC) content of the treated water, giving retentions higher than 99% for COD and 97% for TOC. About 52% of phosphorus was spontaneously precipitated as calcium phosphate (presumably as hydroxyapatite, purity 80%) at the second stage of the process. High turbulence (rotor tip speed 13.7 m/s) at the membrane surface during the second stage tertiary filtration prevented the formation of inorganic scale and membrane fouling. Precipitation occurred in the settling tank after the filtration when the turbulent flow conditions subsided. This enabled the continuation of the filtration to a high VRF value of 300 despite the significant calcium and phosphorus concentrations. The results presented here confirm that shear-enhanced nanofiltration is a promising approach for efficient minimization of the NF concentrate volume, as well as for simultaneous phosphorus recovery without the need for precipitation chemicals.

1   Introduction

Decreasing natural resources, such as fresh water and phosphorus, as well as the need to protect the environment, is increasingly leading to stricter legislation concerning the effluents discharged from wastewater treatment plants (WWTPs). Phosphorus is an important, but unfortunately depleting natural resource. The global production from phosphate rock is estimated to peak around 2033, after which the production will gradually decrease. Therefore, it is important to enhance the nutrient removal and recovery in municipal wastewater treatment in addition to the enhanced purification to enable water reuse. One very promising method for improving effluent quality as well as nutrient removal and recovery is membrane filtration, and especially nanofiltration (NF) and reverse osmosis (RO), which enable the production of highly purified water from municipal wastewater, but also enhanced phosphorus removal. Typically, these processes are carried out in spiral-wound modules that have a high packing density and good cost competitiveness. However, these modules are sensitive to plugging and have limitations concerning their achievable water recovery. Nevertheless, they have been applied in many processes as tertiary treatments, such as in water reclamation, e.g. in a membrane process branded as NEWater process by Singapore's Public Utilities Board, where drinking water is produced from municipal wastewater. The challenge of using spiral-wound modules is that only 50–85% of the feed flow is purified as membrane permeate. The rest of the feed forms a concentrate, which is a voluminous waste stream containing elevated amounts of nutrients and various impurities, such as low molecular weight refractory organic compounds and inorganic salts. In addition, this concentrate often has limited biodegradability. Further treatment of this concentrate can also be demanding due to its very high volume and relatively diluted nature.
 [1–7]

From an environmental and resource recovery point of view, an efficient membrane concentrate management is a major issue of membrane-based wastewater treatment. [6,8–10] Membrane concentrate disposal strategies and regulations have been extensively studied [11,12]. According to Van der Bruggen et al. [12], the traditional concentrate disposal options are incineration or direct or indirect discharge to surface water, ground water, or a landfill, whereas a more beneficial option is recovery of valuable substances from the concentrates before disposal. A relatively concentrated

stream would be highly recommended for efficient recovery of valuable substances from concentrates. However, a low shear rate, thin spacers, and narrow feed channels increase the propensity of spiral-wound modules to clogging by suspended solids or precipitates formed during filtration. Therefore, high concentrations of valuable substances (e.g., nutrients) cannot be achieved using the spiral-wound modules that are traditionally used in tertiary municipal wastewater treatment.

The volume of membrane concentrates can be decreased by shear-enhanced membrane filtration, which simultaneously increases the concentration of valuable substances. Shear-enhanced membrane filtration creates a high turbulence at the membrane surface, which allows a decrease in the concentration polarization, an increase in the permeate flux, and a potential inhibition of membrane fouling [13,14]. A high shear rate at the membrane surface can be generated with moving parts such as rotating discs, rotors, or rotating membranes, or by vibrating the membrane with, for instance, vibratory shear enhanced processing (VSEP) technology [13–16].

VSEP technology has been utilized for several applications, such as landfill leachate treatment [17,18] or reverse osmosis treatment of brackish water concentrate [16]. According to Subramani et al. [16], the water recovery in from brackish water with a high silica content could be increased from 75% (volume reduction factor, VRF, 4) to 94% (VRF 16) using VSEP technology for RO concentrate treatment. They also reported an inhibition of deposition of colloidal silica to the TMG10 Toray membrane by acid treatment of the RO concentrate (pH from 7.4 to 5.0) during VSEP filtration. However, the barium sulfate precipitation still presented a problem and the membrane required frequent cleaning [16].

Another high shear rate technology applied for the treatment of challenging effluents (e.g. from the pulp and paper industry) is cross-rotational (CR) filtration technology [19–22]. The CR nanofiltration process was chosen for use in the present study. A rotating blade in the CR filter provides an extremely high shear rate inside the module; therefore, high VRFs can also be achieved even without the recirculation of concentrate back to the feed required with spiral-wound modules. This means that the concentrate flow rate can be extremely low when the filter is operated at high VRFs.

The high turbulence created by rotors was assumed to prevent the formation of precipitates on the membrane structure and/or to facilitate the removal of possible precipitates from the module by centrifugal forces. In addition, a low flow rate of concentrate would favor a precipitation process outside the module. These advantages were expected to enable extremely high water recovery without significant membrane fouling and module plugging. The feasibility of a novel process concept for further purification of the real MBR effluent by applying a two-stage NF process combined with a settling tank to enable precipitation of phosphorus was evaluated in the present study from the viewpoint of permeate flux and purity, residual concentrate amount, and phosphorus recovery. The membrane concentrate after phosphorus recovery was further purified in our previous study [23] by pulsed corona discharge (PCD) oxidation. The aim of that study was to decrease the amount of micropollutants and to increase biodegradability of the concentrate. In the present study we present an option to minimize the wastewater volume in membrane based tertiary treatment with a simultaneous recovery of phosphorus.

2   Materials and Methods

2.1   Effluents and filtration experiments

The MBR permeate from municipal wastewater treatment (Table 1) was used as feed effluent for the tertiary nanofiltration. The MBR permeate originated from an MBR-activated sludge process operated without chemical phosphorus removal, thereby enabling potential phosphorus recovery from the final NF concentrate (Fig. 1). The MBR pilot provided by Alfa Laval had a polyvinylinedifluoride (PVDF) microfiltration membrane (MFP2) with a pore size of 0.2 µm, membrane area of 8.5 m^2, and average permeability > 500 L/(m^{2}h bar) (data from the manufacturer). The MBR process was operated with an average mixed liquor suspended solids (MLSS) of 10 g/L (8.6–11.1), sludge retention time of 48 days (33–57), and hydraulic retention time of 21 h.

The hydrophilic NF270 membrane (Dow Chemical Company) was used in both nanofiltration stages. The membrane has a cross-linked semi aromatic polyamide active layer on a polysulfone

support. It has a molecular weight cut-off of 220–250 Da and contact angle of 35° (sessile drop method) [24,25]. The NF270 membrane has an isoelectric point of pH 2.7, so the membrane is negatively charged under neutral pH conditions [24].
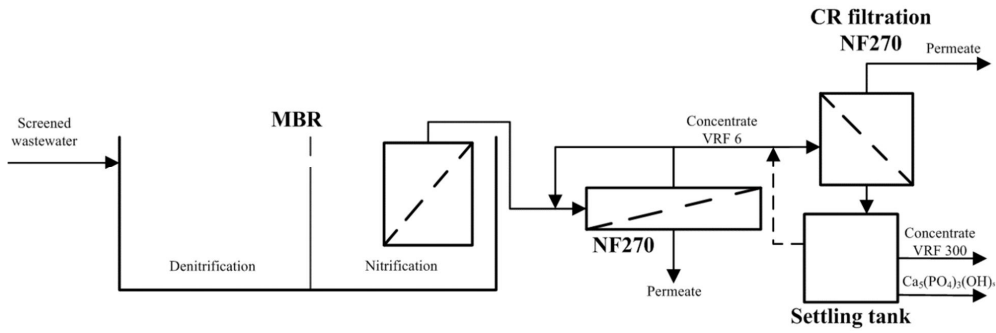

Fig. 1   Municipal wastewater treatment process utilizing shear enhanced nanofiltration (cross-rotational CR350 filter) for the concentrate volume minimization and nutrient recovery.

The first stage nanofiltration was conducted in the 2.5" spiral-wound module (membrane area 2.6 m^2). The average transmembrane pressure was 5.1 bar and the circulation flow rate was 775 L/h (700–800 L/h) in the module. The filtration was carried out for 57 days at an average water recovery of 83% (VRF 6) and the concentrate flow was collected the last 2.5 weeks of spiral wound module operation and sent in 774 L batches on average (7 batches, total volume 5 420 L) for a batch mode concentration filtration (12 days) with a cross-rotational CR350 filter (total membrane area of 1 m^2) to produce the final VRF 300 concentrate (Fig. 1) with a final volume of 110 L. The concentration mode filtration was carried out at a pressure of 4.3 bar and a temperature of 26 °C on average. The concentrate produced in the filtration was circulated back to the feed tank and mixed with the VRF 6 feed. The level of feed tank was kept approximately constant by balancing the addition of fresh feed and permeate output until all batches were added to the feed tank. This was done to provide stable concentration profile during filtration until all feed had been added. After that the filtration was continued by removing permeate and by circulating the concentrate, after removal of precipitates, back to the feed tank.

In the CR filter, the turbulence is generated by rotating a blade (tip speed of 13.7 m/s used) on the membrane surface. This created a high turbulence inside the module, but immediately after the module, the flow conditions subsided in the 1000 L settling tank. The residence time in the settling

tank depended on the volume of concentrate but was more than six minutes through the concentration filtration. The liquid from the settling tank was circulated back to the feed tank. The membranes were cleaned using alkaline (P3-Ultrasil 110, Ecolab) and acidic (P3-Ultrasil 75, Ecolab) cleaning agents.

Table 1   Properties of the MBR permeate used as feed effluent for nanofiltration process with a 2.5" NF270 spiral wound module. [a]The MBR permeate contained various micropollutants; the substances presented in the table are examples of different pollutant types present in the MBR permeate.

Parameter	Feed for NF270 spiral
pH [-]	7.0
Conductivity [μS/cm]	534
TOC [mg/L]	9.5
COD [mg/L]	22
BOD_7 [mg/L]	<2
BOD_7/COD ratio [-]	<0.09
Total phosphorus, P_{tot} [mg/L]	4.4
Total nitrogen, N_{tot} [mg/L]	23
Micropollutants[a]	
Diclofenac [μg/L]	1.1
Carbamazepine [μg/L]	0.6
Furosemide [μg/L]	13.6
Metoprolol [μg/L]	1.2
DEET [μg/L]	0.009

2.2   Analytical procedures

The pH of the samples was analyzed with a Metrohm 744 pH meter (SFS 3021) and conductivity with a Knick Konduktometer 703 (SFS 3022). Dissolved organic carbon (DOC) was analyzed with a Shimadzu TOC-L total organic carbon analyzer. Samples were centrifuged (10 min, 3500 rpm) with the ELMI CM-6MT centrifuge before the DOC analysis. Chemical oxygen demand (COD) analyses were made with the Hach DR2010 spectrophotometer at 420 (low range) or 620 nm (high range) (COD LR/HR, DIN ISO 15705/SFS 5504). Calcium and magnesium ions were analyzed according to the SFS-EN ISO 14911 standard with a Thermo Fisher ICS-1100 ion chromatograph equipped with IonPac CG12A (4×50mm) + CS12A (4×250mm) columns and 22mN H_2SO_4 as the eluent. Biological oxygen demand (BOD_7) measurements were made in a Finas accredited environmental laboratory (T032, SFS-EN ISO/IEC 17025:2005) with a determination limit of 2 mg/L. Total phosphorus was analyzed with the Spectroquant® Phosphate cell test (method analogous to DIN EN ISO 6878) and a Spectroquant Nova 60 spectrophotometer (method 14729, total phosphorus). Total nitrogen was analyzed with the total nitrogen unit (TNM-L) of the

Shimadzu TOC-L total organic carbon analyzer. The precipitate formed during the concentration filtration with CR350 filter was analyzed by scanning electron microscopy (SEM) with a Hitachi SU3500 instrument and by energy dispersive X-ray spectroscopy (EDS) with a the Thermo Scientific UltraDry SDD EDS instrument. SEM images were obtained using a 15-kV acceleration voltage and a BSE detector. The EDS measurement were conducted using a dual detector, a spot size of 1.5×1 mm and Pathfinder software. For the SEM and EDS analyses, a small amount of precipitate was pressed as a cake and measurements were taken from the surface of the cake.

Samples for micropollutant analysis were taken from the first stage nanofiltration process with the 2.5" NF270 spiral-wound module (concentration to VRF 6), as well as from the concentration filtration of the NF concentrate made with NF270 membrane in the CR350 filter (Fig. 1). Samples were collected in 1 L glass bottles and kept at 4 °C until analysis which was initiated within 24 h of sampling. Pharmaceuticals were determined by solid phase extraction and UPLC/MS/MS analysis. The analysis method was based on the EPA 1694 and EPA 539 (modified) standards. The concentration of N,N-Diethyl-meta-toluamide (DEET) was determined using solid phase extraction and GC/MS/MS analysis [26].

2.3 Calculations

Equation (1) was used to calculate the retentions (R, momentary) in the NF stages with the NF feed and permeate values at different VRF values.

$$R = \left(1 - \left(\frac{\text{Ci permeate}}{\text{Ci feed}}\right)\right) \times 100\% \tag{1}$$

where $C_{i\ permeate}$ Value of a specific parameter (i) in the NF permeate at a certain VRF value.

                     $C_{i\ feed}$ Value of a specific parameter (i) in the NF feed/concentrate at a certain VRF value.

Fouling (F) was determined using equation (2) as the percentage drop in the pure water permeabilities due to filtration of wastewater, as follows:

$$F = \left(\frac{PWPa - PWPb}{PWPa}\right) \times \mathbf{100\%} \tag{2}$$

where PWP_a Initial pure water permeability (L/(m²hbar)) before filtration

                   PWP_b Pure water permeability (L/(m²hbar)) after filtration of wastewater.

3   Results and Discussion

3.1   The first stage nanofiltration with a spiral-wound module

The NF270 membrane was chosen as it is a high permeability nanofiltration membrane that has shown a low fouling tendency in wastewater applications. The low fouling tendency often observed for the NF270 membrane is mainly attributed to its low surface roughness and hydrophilic surface (contact angle around 30 °). [24,27–29]

An average permeability of 4.3 L/(m²hbar) (flux 22 L/(m²h), TMP 5.1 bar, 14 °C) was obtained for the first stage nanofiltration with the 2.5" spiral-wound module (Fig. 2). This capacity was similar to that reported by Bellona et al. [27] for the NF270 membrane (4.6 L/(m²hbar) at 25 °C) in a water reclamation process, although the average filtration temperature was lower in the present study. The result was a decreasing effect in the membrane capacity due to water viscosity. The nanofiltration gave a good removal of COD and DOC, with retentions higher than 99% for COD and 97% for DOC, and it removed phosphorus (>95%) (Table 3).
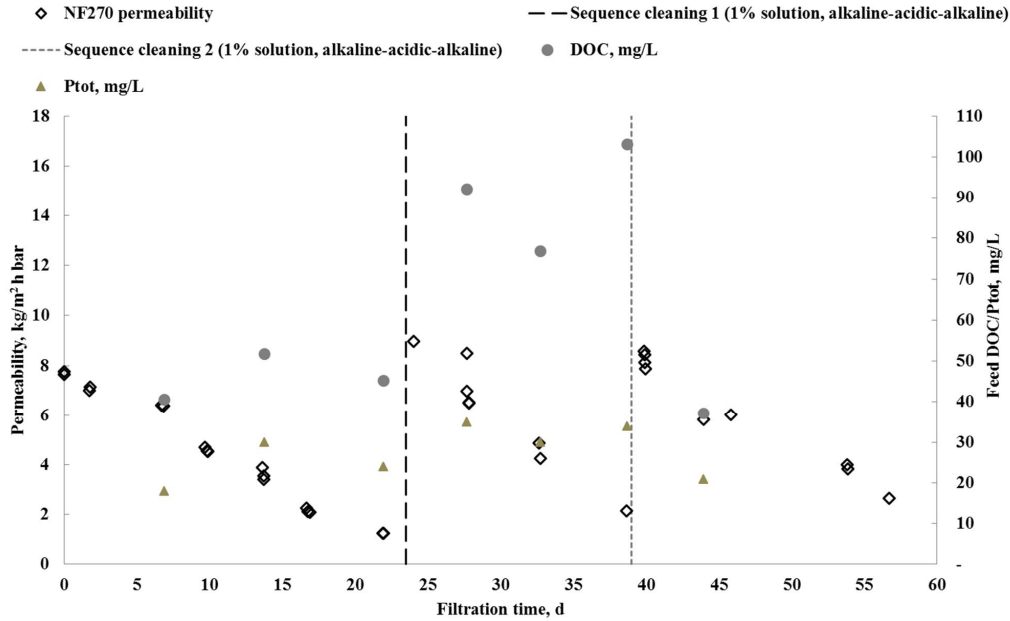
Fig. 2 Permeability and feed effluent (MBR permeate) DOC and P_{tot} as a function of filtration time during a 57-day filtration of MBR permeate using a 2.5" NF270 spiral module. The average temperature in the filtration was 14 °C, flux 22 L/(m²h), transmembrane pressure (TMP) 5.1 bar, volume reduction factor (VRF) 6. Cleaning sequence: alkaline cleaning with 1% P3-Ultrasil 110, acidic cleaning with 1% P3-Ultrasil 75, and alkaline cleaning with 1% P3-Ultrasil 110. Total cleaning time was 60 min for each cleaning (20 min circulation, 40 min soaking), 20–25 °C.

Prominent fouling (>70% pure water permeability decline compared to initial permeability) was observed in the filtration with the spiral-wound module (Table 2). The pressure drop over the spiral-wound module also increased up to 0.7–0.9 bar in the nanofiltration before membrane cleaning sequences were started. This pressure drop was already close to the 1.0 bar limit value for the membrane element used (manufacturer's statement). Therefore, filtration could not have been continued to significantly higher VRF values.

The cleaning experiments with alkaline (P3-Ultrasil 110, Ecolab) and acidic (P3-Ultrasil 75, Ecolab) cleaning agents revealed that the fouling consists of both organic and inorganic compounds. Alkaline cleaning did not completely restore the filtration capacity, and some improvement in permeability was also achieved by acidic cleaning, indicating the existence of inorganic foulants (Table 2). The filtration and cleaning periods were not optimized in the present

study; however, as shown in Fig. 2, the initial fluxes in the filtrations after cleaning were approximately the same, indicating that cleaning was quite effective. The low filtration temperature, being between 9 and 17 °C, might also have increased the fouling tendency of organic compounds, as reported by [29]. Inorganic scaling probably further decreased the filtration capacity, since the feed for the spiral-wound module contained a significant amount of phosphorus (4.4 mg/L) and the filtration was conducted at a VRF 6. This means that the average concentrations of phosphorus and calcium in the circulation loop were 25 mg/L and 76 mg/L, respectively. Bellona et al. [27] reported inorganic scaling as the presumed reason for a 10% flux decrease in the NF270 membrane in a water reclamation process, even though the effluent contained significantly less phosphorus (0.4 mg/l) and calcium (54 mg/l) than was present in our study.

3.2 Concentration filtration with the high shear rate CR module

During the 12-day concentration filtration with the CR350 filter to VRF 300, which was started in the last week of spiral wound module operation, the average permeability was 8.9 L/(m^{2}hbar) (flux 34 L/(m^{2}h), 26 °C; Fig. 3). The effect of shear-enhanced membrane filtration on permeability was significant; an average permeability over two times higher could be reached with the CR350 filter than with the spiral wound module in the first stage nanofiltration, despite the very high final VRF value, at 300. However, the lower temperature in the first stage filtration process (14 vs. 26 °C) partly explains the difference and might also have affected membrane fouling (Table 2). The correction of the average permeability of the first stage NF stage (4.3 kg/(m^{2}hbar) to a temperature of 26 °C using a viscosity correction gave a permeability of 5.9 kg/(m^{2}hbar), which is still significantly lower than the one measured with the shear-enhanced filtration (8.9 kg/(m^{2}hbar)). Consider also that the osmotic pressure was significantly higher for the shear-enhanced filtration than for the first filtration stage, especially for a VRF of 300.
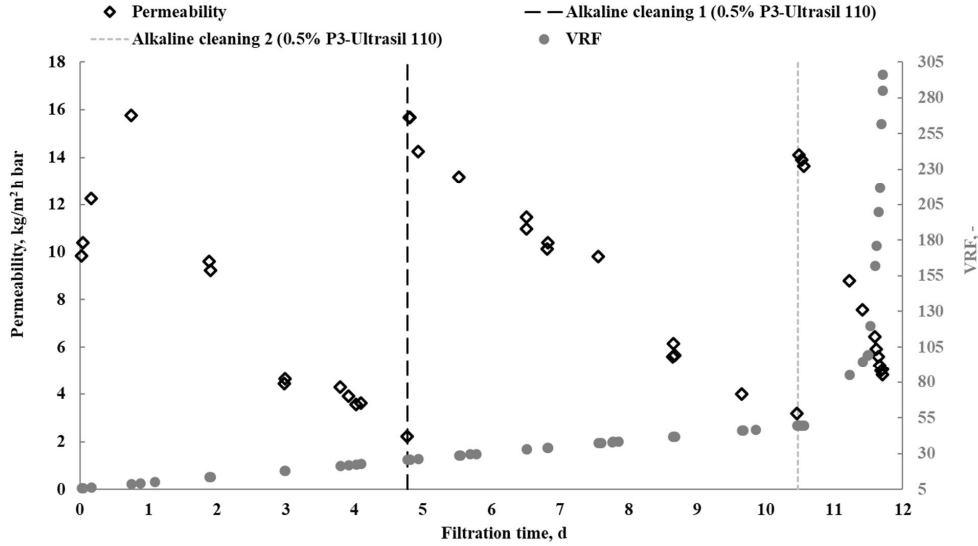
Fig. 3   Permeability and VRF values as a function of filtration time in the concentration filtration of NF270 concentrate with the CR350 filter. The average temperature during the filtration was 26 °C, flux 34 L/(m²h), transmembrane pressure (TMP) 4.3 bar, and rotor speed 750 rpm (13.7 m/s tip speed). The membrane was cleaned with alkaline 0.5% P3-Ultrasil 110 at 35°C for 110 min in total (10 min circulation, 90 min soaking, 10 min circulation).

When compared with the nanofiltration with the spiral-wound module, the concentration filtration with the high shear rate CR350 filter showed a significantly lower or even negligible fouling tendency (Table 2). Furthermore, as Table 2 shows, the minor fouling was completely restored with alkaline cleaning alone. The high shear rate on the membrane surface seemingly prevented scale formation on the membrane surface and fouling due to inorganic compounds. The decreasing filtration capacity during the CR filtration was mainly caused by the increase in osmotic pressure during the concentration filtration (conductivity increased from 1 mS/cm to 12.7 mS/cm). At the end of the experiments, the osmotic pressure was estimated at about 4.9 bar when calculated by assuming that the conductivity originates from Na_2SO_4, whereas the TMP at the end of filtration was 6.7 bar. Permeate flux at the end was 27 L/(m²h). The effective driving force (hydrostatic pressure minus osmotic pressure) was approximately 2 bar. The osmotic pressure corrected permeability was about 13 L/(m²h bar), which is close to the permeability at the beginning of the concentration filtration, indicating a low fouling and a small effect of concentration polarization on the flux when compared to the osmotic pressure.

Table 2 Fouling during the first stage nanofiltration of MBR permeate with 2.5" NF270 spiral module (VRF 6, 57 d) and during concentration filtration of NF270 concentrate with CR350 filter (VRF 6–300, 12 d).

Fouling, %			
Nanofiltration with 2.5" NF270 spiral		Concentration filtration with CR350 filter	
After 22-day filtration	86	After 5-day filtration	15
After sequence cleaning 1	20	After alkaline cleaning 1	-19
After 39-day filtration	79	After 10.5-day filtration	4
After sequence cleaning 2	19	After alkaline cleaning 2	-18
After 57-day filtration	72	After 12-day filtration	-3
After alkaline cleaning	30	After alkaline cleaning 3	-27

Sequence cleaning: alkaline with 1% P3-Ultrasil 110, acidic with 1% P3-Ultrasil 75, and alkaline with 1% P3-Ultrasil 110. Total cleaning time was 60 min for each cleaning (20 min circulation, 40 min soaking), 20–25 °C.
Alkaline cleaning: 1% P3-Ultrasil 110 (spiral-wound module), 26°C, 95 min cleaning (20 min circulation, 75 min soaking) and 0.5% P3-Ultrasil 110 (CR350-filter), 35°C, 110 min cleaning (10 min circulation, 90 min soaking, 10 min circulation).

3.3   Permeate purity

Both nanofiltration processes efficiently retained organic substances, measured as COD and DOC, retentions being on average over 99% for COD and 97% for DOC in both processes (Table 3). Retention (%) was determined as the percentage of a specific parameter, such as COD, retained by the nanofiltration membrane at a certain VRF value. Nanofiltration efficiently retained phosphorus, calcium, and magnesium (Table 3). The concentrations of pollutants of the combined permeate (spiral-wound module, 27 545 L + CR filter, 5 310 L) that would potentially be discharged or reused were clearly below the concentrations achieved with activated sludge process and generally below discharge limits (Table 3). However, this study was made without chemical precipitation of phosphorus in biological treatment; therefore, due to the high concentration of phosphorus in the filtration stages, the combined permeate contained phosphorus at about 0.7 mg/L, which exceeds the discharge limit of some larger municipal wastewater treatment plants in Finland. If necessary, the permeate could be further purified with NF (two-pass NF) to achieve a phosphorus level of about 0.05 mg/L. Obviously, as an alternative a chemical coagulation can also be used to reduce the amount of phosphorus.

The concentration of organic substances measured as DOC and COD increased linearly during concentration filtration toward a final VRF value of 300 (Fig. 4, Table 3). For instance, the COD increased from 22 to 5925 mg/L, corresponding to a concentration factor of 270, which is rather

close to a VRF of 300. The removal of nitrogen was minor, and more than 95% of the total nitrogen was in the combined permeate. This is not surprising, since monovalent ions, such as nitrate, are not efficiently removed in high permeability NF [24].

Micropollutants, such as diclofenac, carbamazepine, furosemide, metoprolol, and DEET, were also efficiently removed with nanofiltration (Fig. 1, Table 3). Retentions for all these pollutants were, on average, above 90%. According to Arola et al. [30], the major separation mechanisms for these micropollutants are size exclusion, hydrophobic/hydrophilic interactions, and electrostatic interactions. For instance, the molecular weights for diclofenac (296.2 g/mol), furosemide (330.7 g/mol), and metoprolol (267.4 g/mol) are higher than the nominal cut-off value of the NF270 membrane (220–250 Da); therefore, these compounds are readily removed. In addition, the pKa values for DEET, diclofenac, and furosemide are <2, 4.2, and 3.8, respectively, indicating the existence of electrostatic repulsion between the membrane and these solutes. Furthermore, the log P values range from 1.9 to 4.5, so all these compounds are somewhat hydrophobic. Therefore, the adsorption of compounds (e.g., carbamazepine with a log P 2.5 and pKa 13.9) onto the membrane structure might also affect their removal efficiency. The analyzed micropollutants were concentrated into the final membrane concentrate, and further concentrate treatment, such advanced oxidation, could be applied to degrade them from the nutrient rich concentrate. [23,24,30]

Table 3 Average values for different parameters of the feed effluent (MBR permeate), as well as the VRF 6 concentrate and permeate during nanofiltration with the NF270 spiral-wound module and temporary values at VRF 300 for the permeate (measured from the permeate pipe) and concentrates from concentration filtration with the CR350 filter. The average temperature was 14 °C, flux 22 L/(m²h), transmembrane pressure (TMP) 5.1 bar, and volume reduction factor (VRF) 6 during the filtration with the 2.5" NF270 spiral-wound module. Concentrate with VRF value 6 was used as a feed for filtration with the CR350 filter. The average temperature was 26 °C, flux 34 L/(m²h), transmembrane pressure (TMP) 4.3 bar, and rotor speed 750 rpm (tip speed 13.7 m/s) during the filtration with the CR350 filter. Final VRF 300.

Parameter	MBR permeate	Concentrate, VRF 6	Permeate, VRF 6	Concentrate, VRF 300	Permeate, VRF 300	Estimated combined permeate from both NF processes
pH, -	7.0	7.1	6.5	5.9	8.5	6.9
Conductivity, µS/cm	534	1 051	444	12 670	581	448
DOC, mg/L	9.5	64	1.8	2 130	5.5	1.9
COD, mg/L	22	176	1.5	5 930	24	2.6
BOD_7, mg/L	<2	<2	<2	74	<2	<2
P_{tot}, mg/L	4.4	25	1.1	380	7.1	0.7
N_{tot}, mg/L	23	19	22	190	20	22
Ca, mg/L	-	76	10	663	15	10.4

|						
Mg, mg/L	-	17	2.2	629	3.7	2.3
Micropollutants[a]						
Diclofenac, µg/L	1.1	6.7	0.15	410	5.0	0.14
Carbamazepine, µg/L	0.6	1.7	0.21	33	2.4	0.15
Furosemide, µg/L	13.6	37	1.50	580	12.0	1.0
Metoprolol, µg/L	1.2	3.4	0.49	78	2.9	0.32
DEET, µg/L	0.009	0.16	<0.005	1.1	0.06	0.004

3.4   Concentration of nutrient ions and DOC

Phosphorus was efficiently concentrated to the final concentrate (VRF 300), with an average retention of about 97%. The pH of the concentrate decreased from 7.1 (VRF 6) to 5.9 (VRF 300), presumably due to the removal of acids, such as carboxylic acids, as also observed as the pH value changes of the permeate (6.5 at VRF 6 to 8.5 at VRF 300) (Table 3). According to Zacharof et al. [31] the negatively charged NF 270 membrane is capable of retaining carboxylic acids, such as acetic acid and butyric acid, during wastewater treatment. Zacharof et al. [31] treated digested agricultural wastewater with an NF270 membrane at neutral pH conditions and achieved as much as 75% retention for acetic and butyric acid.

The concentration of calcium and phosphorus increased steeply in the concentrate up to VRF 50, in a similar manner to that observed for the concentrations of DOC, N_{tot}, and Mg during the filtration from VRF 6 to 300 (Fig. 4a and 4b). The amount of total nitrogen in the concentrate also increased during the concentration filtration, but not as significantly. The total nitrogen consists of inorganic nitrogen (ammonium, nitrate, and nitrite) and nitrogen in organic compounds (e.g. proteins and amino acids). In this wastewater, the inorganic nitrogen was almost completely nitrate. Its concentration was always higher in the permeate than in the feed, which led to an almost nitrate free final concentrate (0.4 mg/L). However, the amount of total nitrogen in the final concentrate increased due to retention of nitrogen in organic compounds, which were retained by the NF.

After the reaching VRF 50, the increase in P_{tot} and Ca concentration was no longer linear with the VRF value (Fig. 4b). Results indicate that phosphorus and calcium began to precipitate when the filtration was carried out further toward a final VRF value of 300. The extremely high shear rate inside the filtration module prevented precipitation inside the module—or if precipitation occurred

inside the module, the centrifugal forces efficiently removed the particles from the module. Therefore, fouling was almost negligible in the concentration filtration (second stage NF). Conversely, when the flow has subsided in the settling tank, the conditions favors precipitation in the saturated solution, and calcium phosphate was precipitated and removed from circulation flow in the concentration process (Fig. 1).
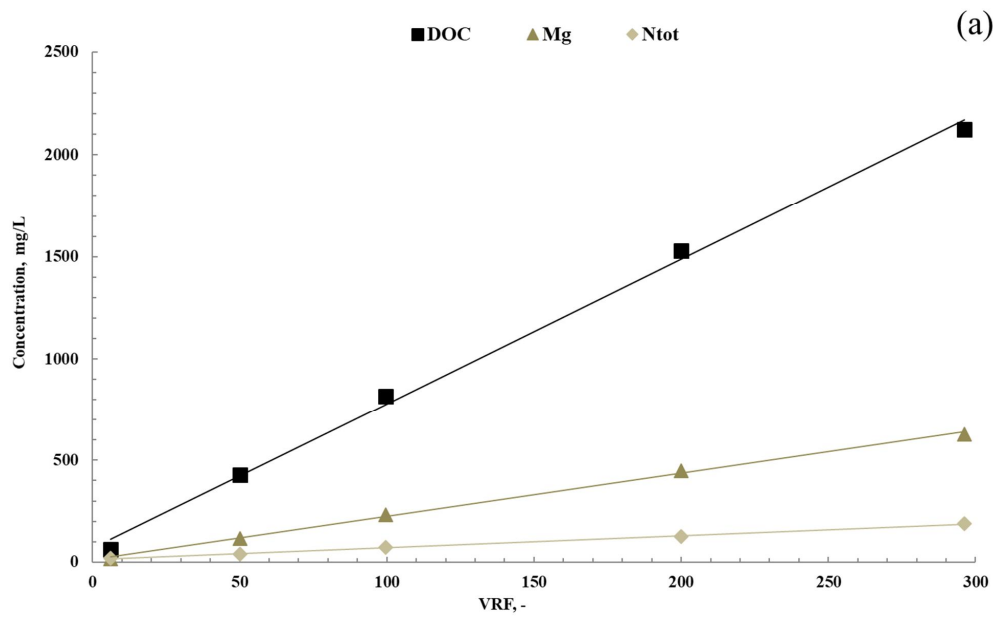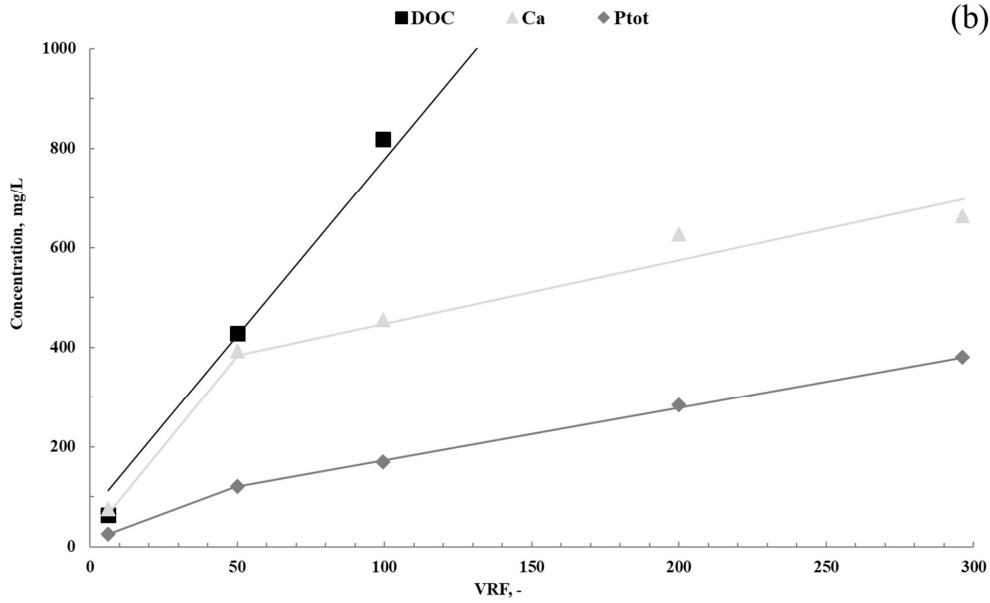
Fig. 4   Concentrations of DOC, N_{tot}, and Mg (a), as well as DOC, P_{tot}, and Ca (b) in the NF270 concentrate as a function of the volume reduction factor (VRF) during a 12-day filtration of NF270 concentrate with the CR350 filter. The average temperature was 26 °C, flux 34 L/(m²h), transmembrane pressure (TMP) 4.3 bar, rotor speed 750 rpm (13.7 m/s tip speed), and VRF from 6 to 300.

3.5   Recovery of phosphorus

As mentioned previously, the concentrations of calcium and phosphorus increased steeply in concentration filtration up to VRF 50 (Fig. 4), after which the rate of increase in concentration changed and concentrations of calcium and phosphorus were no longer increasing so rapidly when filtration was continued further to a final VRF value of 300. This indicates that calcium and phosphorus are partly precipitated. Figure 5 shows the result of EDS analysis of the precipitate. The main elements in the precipitate were oxygen, calcium, and phosphorus, which indicated a precipitation of calcium phosphate. Precipitation of calcium phosphate is usually carried out at elevated pH (above 8.5), since the supersaturation index (SI) of calcium phosphates, being the thermodynamic driving force for precipitation, increases significantly when the pH is increased to above 8 from a neutral pH [32,33]. According to Song et al. [33], hydroxyapatite (HAP; $Ca_5(PO_4)_3(OH)$) is the most likely calcium phosphate phase to be found in the final precipitate, since it has clearly the highest SI value (at a pH range between 5.5 and 12) of the most typical

calcium phosphate phases, such as dicalcium phosphate (DCPD), octacalcium phosphate (OCP), and tricalcium phosphate (TCP). HAP is also thermodynamically the most stable calcium phosphate phase [32].

According to Carlsson et al. [34], even spontaneous calcium phosphate precipitation may be possible at neutral pH in the enhanced biological phosphorus removal process (EBPR), if concentrations in the effluent to be treated exceed 50 mg/L for phosphorus and 100 mg/L for calcium and the COD/P ratio is below 55. In the present study, the concentrations of 50 mg/L for phosphorus and 100 mg/L for calcium were exceeded at around VRF 20 (Fig. 4) in the concentration filtration and the COD/P ratio was below 16 during the second stage NF. In that sense, the precipitation of calcium phosphate observed during the second stage NF was expected to occur when the filtration was carried out beyond VRF 20. Thus, based on the results (Fig. 4 and 5), as well as findings of Carlsson et al. [34], the calcium phosphate started to precipitate between VRF 20 and 50. Lopes et al. [35] have also reported that calcium phosphate can precipitate at pH 6 as HAP, and the presence of organic compounds enhances the formation of HAP crystals with a rosaceous shape. This shape can also be seen in the precipitate from these experiments (Fig. 5).

The pH of the concentrate decreased the from an initial value of 7.1 to 5.9 in the final concentrate (VRF 300) in this study, whereas the concentrations of calcium and phosphorus in the concentrate varied between 374–640 mg/L and 121–380 mg/L, respectively, at VRF 50–300. The spontaneous crystallization of calcium phosphate, likely as rosaceous shaped HAP crystals (Fig. 5), occurred during the filtration of the NF concentrate. Based on the EDS analysis, the Ca/P molar ratio of the precipitate formed during second stage filtration was 1.48, which corresponded to Ca/P molar ratio of amorphous calcium phosphate (ACP) and tricalcium phosphate having a Ca/P molar ratios of 1.2–2.2 and 1.5, respectively [36,37]. However, precipitation of calcium phosphate was unlikely to occur as ACP or TCP, since ACP is not a stable calcium phosphate form and usually acts as a precursor phase for HAP. TCP has a very small supersaturation index under the pH conditions of concentration filtration (TCP SI < 0 at pH 6 and SI < 2 at pH 7) [32,33,37]. Although the Ca/P molar ratio of 1.48 in the precipitate was lower than the stoichiometric Ca/P molar ratio of 1.67 for HAP, the precipitation of calcium phosphate as HAP was likely under the observed filtration conditions.

The precipitation of magnesium ammonium phosphate (MAP) from the concentrate could also be possible, in addition to HAP precipitation, if the concentrations of phosphorus, magnesium, and ammonium were high (>50 mg/L) and the phase ratios between magnesium, phosphorus, and nitrogen were favorable. MAP crystallization could be a feasible method for phosphorus recovery at elevated pH values around 9, given a phase ratio around 1.2–1.6:1 between magnesium and phosphorus and 1–5:1 between ammonium and phosphorus present in the membrane concentrate [38–42]. Thus, based on the results, the precipitation of MAP from the NF concentrate was unlikely, since the pH and initial phase ratios between phosphorus, magnesium, and ammonium were not optimal (Table 3). The concentration of magnesium in the concentrate also increased almost linearly as a function of the VRF value (Fig. 4). Only a minor amount of magnesium was found in the precipitate based on EDS analysis (Fig. 5). The decrease in pH of the concentrate during concentration filtration, from 7.1 to 5.9, could also inhibit the precipitation of MAP in the later stages of filtration, when the phase ratios might be more suitable for MAP precipitation. MAP precipitation is highly dependent on the effluent pH and usually requires a pH above 8 (maximum SI $\geq$ 2 at pH 9) for a notable precipitation, whereas the precipitation of MAP below pH value of 6.5 is negligible (SI <0) [38,39,42].

EDS analysis	
Element	Wt %
O	40.3
Ca	28.5
P	14.9
C	12.9
Mn	0.9
S	0.9
Mg	0.7
Fe	0.7
Na	0.3
Al	0.2
Total	100
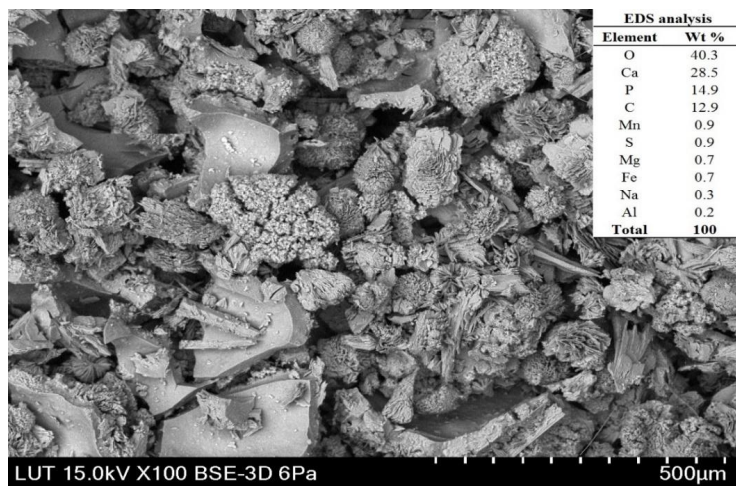
Fig. 5   SEM image and EDS analysis of the precipitate formed during second stage filtration with a CR350 filter. Hitachi SU3500 scanning electron microscope, BSE detector, 15 kV acceleration voltage. Thermo Scientific UltraDry SDD EDS energy dispersive X-ray spectroscope, dual detector, 1.5 X 1mm spot size, Pathfinder software. Calcium phosphate precipitates appear in the figure as "rosaceous structures."

Very high calcium and phosphorus concentrations in the NF concentrate during filtration with CR350 filter (Fig. 4) could increase the membrane fouling tendency by calcium phosphate ($CaPO_4$) scaling. According to Subramani and Jacangelo [43], $CaPO_4$ scaling is one of the main obstacles hindering the increase of the feed water recovery in RO desalination. However, membrane fouling in the CR filtration was almost negligible, based on the pure water permeabilities (Table 2). Therefore, $CaPO_4$ scaling was negligible. One possible reason for very minor fouling and negligible $CaPO_4$ scaling was the high turbulence at the membrane surface due to the rotating blade. Several research groups [44–46] have found that an excessive mixing speed in crystallization may slow down or even stop the crystal growth, while also increasing the breakage of the crystals already formed. The rotating blade with a 13.7 m/s tip speed might have caused a similar effect to that of high mixing speed in the crystallization applications. In addition, if precipitation occurred inside the CR-module, the centrifugal forces would efficiently remove the particles from the module. Thus, the precipitation of calcium phosphate into the NF270 membrane structure was prevented in this study.

After the CR350 module, the concentrate flowed into a settling tank, where calcium phosphate precipitated and settled to the bottom of the tank and the liquid was circulated back to the filter (Fig. 1). Therefore, concentration filtration could be continued to the high VRF value of 300 regardless of the high calcium and phosphorus concentrations. This concept of the use of very high turbulence inside a membrane module and significant centrifugal forces can be potentially useful in other applications where precipitation needs to be prevented during saline water treatment, as described previously [47]

Based on the EDS results (Fig. 5), around 80% of the precipitate weight content was calcium phosphate when estimated as HAP (Ca/P ratio 1.67). The recovered precipitate could potentially be used as such for fertilizer applications due to the high purity of HAP (~80%) in the precipitate. The EDS analysis shown in Fig. 5 reveals low amounts of metals, such as manganese, magnesium, iron, and aluminum. The phosphorus and calcium mass balances indicate that about 52% of the phosphorus and 60% of the calcium were precipitated and recovered as solid material in the studied process concept (Fig. 1). The final NF concentrate (VRF 300) still contained 380 mg/L of

phosphorus and 189.5 mg/L of nitrogen, as well as calcium (663 mg/L) and magnesium (629 mg/L). This concentrate (VRF 300) could also be potentially utilized as a liquid fertilizer after a feasible treatment, such as advanced oxidation, that would degrade micropollutants present in the concentrate (Table 3, [23]). The phosphorus recovery from this concentrate (VRF 300) potentially as HAP at an elevated pH of 9.5 could be another option to obtain further increases in the overall phosphorus recovery rate. According to Arola et al. [48], 98% recovery of phosphorus can be achieved from the NF270 concentrate (VRF 300) by chemical precipitation with $Ca(OH)_2$ (1.4 g/L dose) at pH 9.5; thus, recovery of nearly all the phosphorus is possible from the NF concentrate.

In this non-optimized treatment concept, approximately 86% of the phosphorus present in the feed for the NF270 spiral (MBR permeate, P_{tot} 4.4 mg/L) was recovered either in the form of a precipitate (HAP, about 80% purity, 52% of the P_{tot}) or in the concentrated liquid (in the final NF concentrate, 34% of the P_{tot}), from where it can be utilized, as discussed above. This was achieved without the use of any precipitation chemicals. The final VRF value of 300 was very high compared to traditional VRF values of 2–7 obtained in water reclamation plants [8,9]. Two-stage nanofiltration utilizing shear-enhanced membrane filtration as a form of cross-rotational CR350 filter in the second stage therefore appeared to be a promising approach for efficient concentrate management, waste minimization, and phosphorus recovery.

4   Conclusions

Municipal wastewater treated with an MBR process without addition of phosphorus precipitation chemicals was further purified in a novel two-stage NF process using spiral-wound NF and high shear-rate CR-nanofiltration to minimize the amount of final concentrate and to recover phosphorus. The CR -module construction prevents precipitation of phosphorus compounds inside the module due to extremely high shear rate but favors precipitation of phosphorus outside the module in the settling tank, where almost zero shear rate conditions exist.

In this study, a high VRF value of 300 for the concentrate was achieved using the 2.5" NF270 spiral-wound module (filtration to VRF 6, average permeability 4.3 L/(m^2h bar)) in the first stage, followed by concentration filtration (second stage NF) with the high shear rate CR350 filter

(average permeability 8.9 $L/(m^2h\ bar)$). The process efficiently removed organic substances, measured as COD and TOC, with retentions of over 99% for COD and 97% for TOC. More than 90% removal of the micropollutants diclofenac, carbamazepine, furosemide, metoprolol, and DEET was achieved. Thus, a high-quality effluent could be produced with this process, despite the very high VRF value.

The concentrations of phosphorus, nitrogen, calcium, and magnesium increased significantly in the second stage NF (i.e., 380 mg/L P_{tot}, 180 mg/L N_{tot}, 663 mg/L Ca, and 629 mg/L Mg in the VRF 300 concentrate). Although spontaneous precipitation of calcium phosphate occurred in the settling tank during the second stage NF, the extent of membrane fouling was very minor. The precipitate mainly consisted of HAP, with a purity around 80%. This precipitation enabled 52% recovery of phosphorus from the MBR permeate. A high rotor tip speed (13.7 m/s) in the CR350 filter created a high turbulence at the membrane surface, which prevented the deposition of an inorganic scale on the membrane. Intensive stirring also inhibited fouling by organic compounds. In this non-optimized treatment concept, approximately 86% of the phosphorus was recovered either as a precipitate (HAP, purity ~ 80%, 52% of the P_{tot}) or in the concentrated liquid (34% of the P_{tot}). Thus, the process concept including spiral-wound nanofiltration followed by shear-enhanced nanofiltration with a CR filter appears to be a promising chemical-free process concept for simultaneous effluent purity improvement and membrane concentrate volume minimization, as well as for concentration and recovery of phosphorus.

Acknowledgments

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Publication IV

Kimmo Arola, Mari Kallioinen, Satu-Pia Reinikainen, Henry Hatakka, and Mika Mänttäri
Advanced treatment of membrane concentrate with pulsed corona discharge

Advanced treatment of membrane concentrate with pulsed corona discharge

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ABSTRACT

The aim of this study was to examine the feasibility of pulsed corona discharge (PCD) oxidation for treatment of the nanofiltration concentrate from a municipal wastewater treatment plant. The concentrate studied contained high concentrations of micropollutants, since it was produced in the two stage nanofiltration process and filtered to a very high volume reduction factor of 300. The goal of the PCD treatment was to decrease the amount of micropollutants and to increase biodegradability of the concentrate. The energy dose (10 kWh/m^3) used in the PCD treatment was sufficient to reduce 21% of organic carbon present in the concentrate. However, the PCD treatment degraded efficiently some of the target micropollutants: higher than 92% degradation of diclofenac, carbamazepine, citalopram and furosemide was reached. Degradation rate of the beta-blockers (bisoprolol, sotalol, metoprolol) as well as ketoprofen and N,N-diethyl-meta-toluamide (DEET) was lower: 82, 51, 33, 44 and 50% respectively. The BOD$_7$/COD ratio of the NF concentrate was also increased 3.7 times due to the oxidation.

Based on a linear regression analysis, molecular weight of the micropollutants, the amount of double bonds in their structure and the hydroxyl radical degradation constant were identified as the determining parameters for the degradation rate of the micropollutant in the PCD oxidation. This lead to a conclusion that presence of hydroxyl radicals was more critical for the degradation of the micropollutants than the presence of ozone under the examined conditions.

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1. Introduction

The insufficiency of conventional activated sludge processes for removing hardly biodegradable micropollutants and the environmental risks associated to these pollutants has led to studying of the capability of the advanced treatment processes, such as nanofiltration (NF), reverse osmosis (RO) and advanced oxidation (AOP), to remove them [1–3]. Typically in NF and RO about 15–50% from the feed volume (corresponds to volume reduction factor, VRF, values from 7 to 2) is left as a dilute waste stream called as membrane concentrate. This concentrate contains increased amounts of low molecular weight refractory organics and harmful micropollutants, such as carbamazepine and diclofenac, and has a very limited biodegradability (BOD$_5$/COD ratio <0.05) [4–7].

Degradation of the harmful micropollutants and increase of biodegradability of the concentrate produced in the tertiary NF or RO treatment could be reached with the advanced oxidation processes (AOP) [2,4,8]. For instance, Urtiaga et al. [8] showed over 95% degradation of furosemide, hydrochlorothiazide and caffeine

with the electrochemical oxidation of reverse osmosis concentrate (boron-doped diamond electrode, flow rate 10 L/min, applied current 20–100 A/m^2). Moreover, Miralles-Cuevas et al. [2] obtained over 90% degradation of carbamazepine, ibuprofen and sulfamethoxazole in the photo-fenton oxidation of nanofiltration concentrate (solar energy 2 kJ$_{UV}$/L, H$_2$O$_2$ dose 1.5 mM/L, Fe^{3+} dose 0.1 mM/L). According to Umar et al. [4] the biodegradability of reverse osmosis concentrate can be more than doubled with UVC/H$_2$O$_2$ oxidation (UV fluence 36 mJ/cm^2, H$_2$O$_2$ dose 3 mM/L).

Challenging aspects related to many AOPs are either, high operational costs due to the energy consumption or chemicals used, or high investment costs due to the complex processes [1–3,9]. In order to enhance the cost efficiency of AOPs, a non-thermal plasma method called pulsed corona discharge (PCD) has been developed. The PCD oxidation is a chemical free oxidation method and according to Panorel et al. [10] it has potential for commercial scale applicability due to simple yet effective way to generate in situ strong oxidants such as hydroxyl radicals and ozone, but also due to the simple design of equipment. The PCD oxidation has been shown to degrade pharmaceuticals such as diclofenac from model water solutions [10–12]. However, until now the research related to the

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PCD treatment has been done mainly with model solutions of micropollutants rather than real wastewaters.

The aim of this study was to examine the feasibility of the PCD treatment for the purification of a real nanofiltration concentrate from a municipal wastewater treatment plant. The aim was to degrade micropollutants and to increase biodegradability of the concentrate with the PCD treatment. Moreover, the most important molecular properties affecting the degradation of micropollutants in the PCD oxidation were identified by a regression analysis.

2. Materials and methods

2.1. Feed effluent

A NF concentrate (Table 1) for the PCD treatment originated from a pilot scale municipal wastewater treatment process (Fig. 1). A MBR pilot equipment provided by Alfa Laval contained a polyvinylidene fluoride (PVDF) microfiltration membrane MFP2 with a pore size of 0.2 μm and average permeability >500 L/(m² - h bar) (data from manufacturer). The MBR was operated without chemical phosphorus removal. The two stage nanofiltration with the NF270 membrane (DOW) produced a concentrate with a VRF of 300 (Table 1). The first stage nanofiltration (to a VRF 6) was done with a 2.5″ spiral wound module and the final concentration of the NF concentrate to a VRF of 300 was done by a shear enhanced membrane filtration in a cross rotational CR350 filter [13]. The NF270 membrane with a MWCO of 220–250 Da and a contact angle of 30° has a cross-linked semi aromatic polyamide active layer on a polysulfone support [14,15].

2.2. Pulsed corona discharge oxidation

A non-thermal plasma method in a form of gas phase pulsed corona discharge (PCD) was used for the treatment of the NF concentrate (Table 1). Degradation of micropollutants occurred in a PCD reactor, where ozone and ·OH radicals were generated from oxygen and water by using small energy input from a pulse generator. The high voltage pulse generator created short-term electric pulses (100 ns), which were discharged inside the PCD reactor via electrode wire. The PCD reactor, having a volume of 0.034 m³, utilizes conventional wire-plate corona geometry, where stainless steel electrode wires (0.5 mm diameter, placed 30 mm distance from each other) are horizontally positioned between vertical grounded plate electrodes (placed 17 mm distance from the wires). The discharge propagates in the gap between the electrodes, where the highly reactive oxidants are formed in the plasma. The membrane concentrate was pumped to the top of the PCD reactor and dispersed to the reactor by a simple perforated plate. The concentrate flowed in jets and droplets inside the reactor between electrodes to the zone of the gas-phase pulsed corona discharge formation, where the organic target compounds contacted with the ozone and ·OH radicals [10,12,16].

Strong oxidants created in the PCD oxidation will react readily with the organic compounds present in the solution and degrade them into oxidation products such as carboxylic acids. Oxygen atmosphere was used in the oxidation instead of air atmosphere, since oxygen atmosphere enables enhanced generation of ozone and hydroxyl radicals and therefore increases degradation of organic molecules. The increase in the energy consumption due to the production of oxygen atmosphere was expected to be minor compared to the use of air atmosphere [10,12,17]. More detailed description about the PCD equipment used has been given by Panorel et al. [10].

50 L sample of NF concentrate was poured to the feed tank of the lab scale PCD setup and oxidized at room temperature (20 °C). Oxygen was introduced to the feed tank before oxidation experiment to achieve an average oxygen concentration of 89% inside the PCD reactor during oxidation. The recirculation flow rate in the PCD reactor was 15 L/min to provide sufficient trickling of

Table 1
Properties of the NF concentrate (VRF 300) used as the feed solution for the PCD oxidation and process conditions in the PCD oxidation.

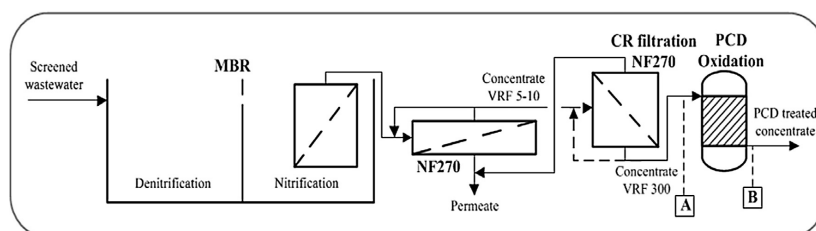| Feed for the PCD oxidation		Conditions during oxidation	
Parameter	NF concentrate	Parameter	PCD oxidation
pH, –	5.9	Pulse repetition frequency, pps	840
Conductivity, μS/cm	12 670	Pulse duration, ns	100
Dissolved organic carbon (DOC), mg/L	2130	Pulse amplitude, kV	20
Chemical oxygen demand (COD), mg/L	5930	Liquid flow rate, L/min	15
Biochemical oxygen demand (BOD₇), mg/L	74	Average atmosphere composition,% O₂	89
BOD₇/COD ratio, -	0.01	Oxidation energy, kWh/m³	0, 0.3, 0.7, 1.5, 3.5, 10
Total phosphorus (P$_{tot}$), mg/L	360	Oxidation time, min	0, 3.5, 8, 17, 38, 102
Total nitrogen (N$_{tot}$), mg/L	180		
Micropollutants			
Beta-blockers, μg/L	35–78		
Mood drugs, μg/L	18–33		
Diclofenac, μg/L	410		
Furosemide, μg/L	580		

Fig. 1. Municipal wastewater treatment process with the PCD oxidation. Sampling points marked as A and B.

concentrate droplets from perforated plate to the PCD reactor. Total oxidation time was 102 min. Six samples were taken during the oxidation experiment, each responding to one oxidation energy (Fig. 1, Table 1).

2.3. Target pollutants and analysis methods

Nine different micropollutants, all pharmaceuticals, were analyzed in this study (Table 2). All samples were collected in a 1 L glass bottles during 102 min oxidation period and kept at 4 °C before analysis. Analysis of samples was started within 24 h of sampling. All pharmaceuticals were determined by using solid phase extraction as a pretreatment method and ultra performance liquid chromatography coupled with mass spectrometry (UPLC/MS/MS) analysis for the micropollutant identification. Analysis method is based on the standards EPA 1694 and EPA 539 (modified) [18]. Least squares linear regression analysis (Microsoft excel 2013, data analysis) was utilized to identify the determining parameters for the micropollutant degradation. Linear regression, such as least squares regression, is a simple and widely used tool to explain the relationships between one dependent and few independent variables such as relation of micropollutant properties to pollutant biodegradation [19–21].

Spearman's rank correlation factor (r_s) was utilized to find the correlations between micropollutant properties and pollutant degradation rates (measured as slope, k,% of degradation to energy dose). Spearman's rank correlation factor (r_s) is a nonparametric statistical tool to measure a monotonic relationship between paired data. According to Krebel et al. [22] it can be utilized in wastewater treatment applications for instance to find correlations between wastewater parameters and oxidation by-products. The strength of the correlation can be interpreted as follows: r_s = 0.0 no correlation, r_s = ±0.2 weak correlation, r_s = ±0.5 moderate correlation, r_s = ±0.8 strong correlation and r_s = 1.0 perfect correlation [23]. The direction of the relationship is defined by the sign of the correlation coefficient (±) and absolute value gives indication about the strength of the correlation [23].

pH of the samples was analyzed by Metrohm 744 pH Meter (SFS 3021) and conductivity by Knick Konduktometer 703 (SFS 3022). Dissolved organic carbon (DOC) was analyzed by using Shimadzu TOC-L total organic carbon analyzer. Samples were centrifuged (10 min, 3500 rpm) with ELMI CM−6MT centrifuge before DOC analysis. COD analyses were made with Hach DR2010 spectrophotometer at 420 or 620 nm (COD LR/HR, DIN ISO 15705/SFS 5504). Analyses for total nitrogen and phosphorus as well as biological oxygen demand (BOD_7) were made in FINAS accredited environmental laboratory (T032, SFS-EN ISO/IEC 17025:2005). Determination limits were 2 μg/L for total phosphorus, 200 μg/L for total nitrogen and 2 mg/L for BOD_7, respectively.

3. Results and discussion

3.1. Degradation of micropollutants

Higher than 92% degradation rate was reached for diclofenac, carbamazepine, citalopram and furosemide in the PCD oxidation studied here (oxidation energy 10 kWh/m³) (Fig. 2). The efficiency of the PCD treatment is based on the oxidation caused by hydroxyl radicals and ozone. Especially the substances having a benzene ring based structure, such as carbamazepine and diclofenac, have an electron rich site for oxidation reactions and will in most cases degrade readily to oxidation by-products [10–12,26]. The NF concentrate treated in this study was concentrated to a very high VRF value of 300 and thus it contained a high amount of organic substances (5930 mg/L of COD, 2130 mg/L of DOC), which com-

Table 2

Characteristics of the target pollutants. pKa values are given at 25 °C. ·OH radical reaction rates given as L/mol/s are estimated from experiments in purified water. Rate constants for the reaction with ozone (k_{O3}) are given at 20 °C and pH of 7.

| Micropollutant	Classification	Formula	Molecular weight, g/mol	pKa, –	log K$_{ow}$, –	k$_{O3}$, M⁻¹ s⁻¹	·OH radical reaction rate, L/mol/s	Double bonds in molecule structure
Ketoprofen	Pain killer	$C_{16}H_{14}O_3$	254.3 [24]	4.5 [24]	3.1 [24]	0.4 [25]	1.5×10^1 [26]	8 [24]
Diclofenac	Non-steroidal anti-inflammatory drug	$C_{14}H_{11}Cl_2NO_2$	296.2 [24]	4.2 [24,27]	4.5 [24,27]	~1 × 10⁶ [28]	8.2×10^9 [26]	7 [24]
Carbamazepine	Anti-epileptic agent and mood stabilizer	$C_{15}H_{12}N_2O$	236.3 [24]	13.9 [24]	2.5 [24,29]	~3 × 10⁵ [28]	9.5×10^9 [26]	8 [24]
Citalopram	Antidepressant and drug for alcoholism	$C_{20}H_{21}FN_2O$	324.4 [24]	9.59 [30]	3.5 [24]	–	–	6 [24]
Bisoprolol	Cardioselective beta blocker	$C_{18}H_{31}NO_4$	325.4 [24]	9.4 [31]	1.9 [24]	–	3.5×10^9 [32]	3 [24]
Metoprolol	Selective beta blocker	$C_{15}H_{25}NO_3$	267.4 [24]	9.7 [33]	1.9 [24]	2×10^3 [28]	8.1×10^9 [26]	3 [24]
Sotalol	Beta-antagonist	$C_{12}H_{20}N_2O_3S$	272.4 [24]	8.4 [34]	0.24 [24]	1.9×10^4 [28]	7.9×10^9 [26]	3 [24]
Furosemide	Loop diuretic	$C_{12}H_{11}ClN_2O_5S$	330.7 [24]	3.8 [24]	2.0 [24]	6.8×10^1 [28]	1.1×10^{10} [26]	8 [24]
N,N-diethyl-meta-toluamide (DEET)	Pesticide, insect repellent	$C_{12}H_{17}NO$	191.3 [24]	<2 [35]	2.0 [24]	0.126 [36]	4.95×10^9 [37,38]	4 [24]
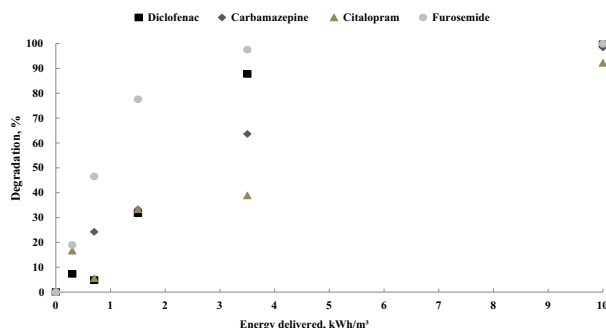
Fig. 2. Degradation of diclofenac, carbamazepine, citalopram and furosemide in the pulsed corona discharge (pulse repetition frequency 840 pps) oxidation of VRF 300 nanofiltration concentrate.
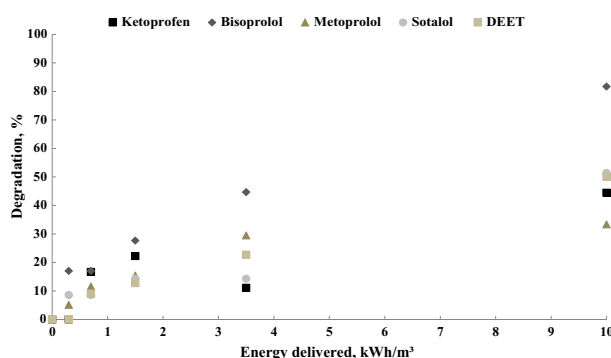

Fig. 3. Degradation of beta blockers bisoprolol, metoprolol and sotalol as well as ketoprofen and DEET in the pulsed corona discharge (pulse repetition frequency 840 pps) oxidation of VRF 300 nanofiltration concentrate.

peted from the oxidants with the micropollutants [1]. Consequently, a significant oxidation energy of 10 kWh/m³ was required to obtain efficient degradation results. However, Arola et al. [39] have shown that an order of magnitude lower oxidation energy (0.2 kWh/m³) was sufficient in the PCD treatment to degrade over 95% of metoprolol, sotalol, diclofenac, carbamazepine and furosemide from the MBR permeate, which contained only small amount of organic compounds (16 mg/L of COD, 7.7 mg/L of DOC).

As Fig. 2 shows, diclofenac, carbamazepine, citalopram and furosemide degraded efficiently in this study, but the decrease in the dissolved organic carbon (DOC) content due to the oxidation treatment was only 21%. According to Dobrin et al. [11], diclofenac will degrade in the PCD treatment to relatively harmless carboxylic acids such as acetic, formic and oxalic acid. Similar degradation behavior from active compounds to carboxylic acids in the PCD treatment has been reported also for other pollutants such as ibuprofen and paracetamol [10,12].

As seen from Fig. 3, degradation rates of beta-blockers as well as ketoprofen and N,N-diethyl-meta-toluamide (DEET) were more modest compared to the other target micropollutants (Fig. 2). Degradation rates between 33 and 82% were observed for these micropollutants (Fig. 3) in the PCD oxidation (10 kWh/m³), the highest observed for bisoprolol. The lowest degradation rates,

being 50, 44 and 33%, were observed for DEET, ketoprofen and metoprolol which had the smallest reaction rates with ozone from the studied micropollutants (Table 2). This could indicate that direct ozonation of DEET, ketoprofen and metoprolol may be inefficient [40]. Potentially recalcitrant nature towards ozone may partly explain the moderate degradation rate of beta blockers as well as ketoprofen and DEET in the PCD oxidation. Longer oxidation time (>102 min) and higher oxidation energy (>10 kWh/m³) is needed for these pollutants to reach degradation rates above 90%. The degradation rate of the specific micropollutants did not always increase in the same order as their ozone reaction rate constants. Consequently, obviously also other factors, such as hydroxyl radical reaction rate and molecular structure, have also a significant impact to the degradation rate of target pollutants in the PCD oxidation. To be able to identify the determining factors for micropollutant degradation in this case, a linear regression analysis was used.

3.2. Determining variables for micropollutant degradation

Factors related to molecular properties affecting degradation were studied with statistical regression analysis. The experiments as such were not aiming at a (physical) parametric model, but

Table 3
Correlation matrix, utilizing Spearman's rank correlation factor (r$_s$), between micropollutants degradation rate (slope, k) and pollutants molecular properties. Citalopram excluded from the analysis due to insufficient data.

	k	k$_{O3}$	·OH radical reaction rate	Molecular weight	pKa	Log K$_{ow}$	Double bonds
k	1	0.21	0.50	0.44	−0.22	0.14	0.62
k$_{O3}$	0.21	1	0.20	0.52	−0.17	0.12	0.44
·OH radical reaction rate	0.50	0.20	1	0.19	0.37	−0.07	−0.06
Molecular weight	0.44	0.52	0.19	1	−0.29	−0.58	0.43
pKa	−0.22	−0.17	0.37	−0.29	1	0.05	−0.14
Log K$_{ow}$	0.14	0.12	−0.07	−0.58	0.05	1	0.16
Double bonds	0.62	0.44	−0.06	0.43	−0.14	0.16	1

instead a preliminary assessment of feasibility of the PCD method as part of hyphenated municipal wastewater treatment technology. Thus with non-parametric regression analysis, the statistics was applied to confirm the conclusions revealed by the experimental results. Degradation rate of each pollutant were computed as a slope (k) for degradation at the low energy dose, i.e., at most linear range of dependence (Supplementary data, S1). These slopes (% of degradation to energy dose) were utilized together with micropollutant properties. Physicochemical properties and molecular structure hold the keys in understanding the phenomena behind the results. Table 3 shows Spearman's rank correlation factors revealing most significant factors effecting on the slope. Cross correlation between the descriptors might bias the result, if the descriptor variables have strong correlation with each another. Therefore the inner correlation structure of all variables is essential to investigate. Table 3 revealed a moderate correlation between some of the descriptors, e.g., Log K$_{ow}$ and Molecular weight (r$_s$ = −0.58), which might increase the risk of biased result/conclusion.

·OH radical reaction rate and molecular weight gave a moderate positive correlations (0.50 and 0.44) with the degradation rate (slope, k) whereas the amount of double bonds gave the strongest positive correlation with the degradation rate (0.62, Table 3). In other words the degradation rate of micropollutants measured by slope (k) was higher for molecules having a high hydroxyl radical reaction constant, molecular weight and high amount of double bonds in the molecule structure. These three parameters were included to the linear least squares regression analysis as descriptors to explain degradation portion slope (Fig. 4).
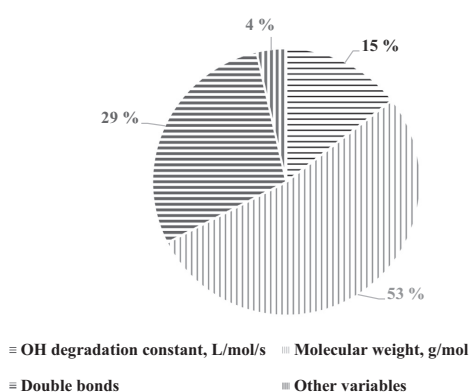

Fig. 4. Importance of different variables to micropollutant degradation rate (slope, k) in the PCD oxidation of the VRF 300 nanofiltration concentrate. Result of the regression analysis. Citalopram excluded from the analysis due to insufficient data.

The result of regression analysis showed that the degradation result in PCD oxidation was dominated by few factors. 96% of the variation of degradation rate of micropollutants in the PCD oxidation could be explained by these three parameters (Fig. 4): molecular weight of the molecule (53%), the amount of double bonds in the molecule (29%) and ·OH radical reaction rate constant (15%). Thus, only 4% of variance could not be explained. This residual term contains the uncertainty of measurements as well as the effect of other factors affecting to the degradation phenomena. It can be concluded that other parameters, such as ozone reaction constant, had relatively small influence to the micropollutant degradation in the pulsed corona discharge. According to Panorel et al. [16] and Ribeiro et al. [41] the performance of advanced oxidation such as the PCD oxidation is claimed to be based on the formation of highly reactive radicals, mainly hydroxyl radicals and ozone. According to Preis et al. [42] the effect of hydroxyl radicals to the oxidation is increased and they have a strong influence on overall oxidation result when higher pulse repetition frequencies are used in oxidation whereas the impact of ozone is stronger in lower pulse repetition frequencies. In this study a high pulse repetition frequency of 840 pps was used. Thus, the result, that the hydroxyl radicals have a more significant impact on the degradation of the target micropollutants compared to ozone, is logical.

3.3. Organic compounds and biodegradability

The PCD oxidation had a relatively small effect to the amount of COD of the treated wastewater concentrate. A COD decrease from 5930 to 5180 mg/L was measured due to the oxidation. The similar behavior was observed with DOC, which decreased from 2130 mg/L to 1670 mg/L. According to Luis et al. [43] the complete mineralization to carbon dioxide and water in AOP occurs only for simple molecules and, consequently, usually only a partial degradation to oxidation by-products is achieved. Based on the pH and DOC results as well as degradation results (Figs. 2 and 3) the strong oxidants, hydroxyl radical and ozone, generated in the PCD oxidation degraded the target micropollutants and other organic compounds presumably to oxidation by-products such as carboxylic acids (pH decrease during oxidation from 5.9 to 5.3) and complete mineralization did not necessarily take place but different kind of oxidation products are formed. For instance, decrease of pH indicates the formation of carboxylic acids. This has also been observed by Panorel [17]. She concluded that the pH decrease during PCD oxidation was a result of the low molecular weight carboxylic acid formation from the cleavage of the benzene rings present in the organic target compounds.

The PCD oxidation had an increasing effect to the biodegradability of NF concentrate; BOD$_7$ value increased from 70 mg/L to 240 mg/L with oxidation. The BOD$_7$/COD ratio was improved from 0.01 to 0.05 with the PCD oxidation. This increase in the biodegradability was 3.7 times based on the BOD$_7$/COD ratio, which was in a similar level compared to the 1.8–3.5 increase in the BOD$_5$/COD ratio obtained by Lee et al. [44] with the ozonation of RO concen-

trate (3–10 mg O_3/L). The recyclability of NF concentrate (VRF 300) back to biological processes (MBR, Fig. 1) was thus enhanced by the PCD treatment. However the achieved biodegradability with the PCD treatment was still limited (BOD_7/COD ratio 0.05) compared to the BOD_7/COD ratio of 0.3 which is considered to be the limit value between biodegradable and biorefractory [7]. Higher oxidation energy would have been required in the PCD oxidation (energy dose above 10 kWh/m^3) in order to make the concentrate completely biodegradable. Direct comparison of the results presented in this study with literature related to energy consumption cannot be made due to remarkable difference in water matrix (in this study the membrane concentrate was significantly more concentrated compared to the existing literature). However, based on the oxidation studies made with model substances such as lignin and humic compounds the PCD oxidation was shown to surpass the energy efficiency of ozonation at least by a factor of two [16,45]. Thus, PCD oxidation can be considered as promising technology also energy consumption wise for the advanced treatment of membrane concentrate.

4. Conclusions

Modern advanced oxidation method as a form of gas phase pulsed corona discharge (PCD) was examined for the degradation of pharmaceuticals and biodegradability enhancement of the real NF concentrate. The concentrate was produced by filtering the permeate from an MBR process with the NF270 nanofiltration membrane to a very high volume reduction factor (VRF) of 300.

This study demonstrates that the PCD oxidation is as promising alternative for advanced membrane concentrate treatment. Higher than 92% degradation of diclofenac, carbamazepine, citalopram and furosemide was reached in the PCD oxidation (energy dose 10 kWh/m^3). Degradation of beta-blockers (bisoprolol, sotalol, metoprolol) as well as ketoprofen and DEET was more moderate; the lowest degradation being only 33% for metoprolol and 44% for ketoprofen, respectively. The concentrate biodegradability measured as BOD_7/COD ratio could be also increased 3.7 times due to the PCD oxidation (from 0.01 to 0.05).

Based on the linear regression analysis molecular weight of the micropollutant, the amount of double bonds in the molecule structure as well as hydroxyl radical degradation constant were the main parameters affecting the degradation rate of the target micropollutants in the PCD oxidation. The degradation of target micropollutants was observed to be more dependent on the presence of hydroxyl radicals than ozone in the conditions used. It can be concluded that the micropollutants, which have a high molecular weight and many double bonds in their structure, and which also are reactive towards hydroxyl radicals, are readily degraded in PCD oxidation using high pulse repetition frequency of 840 pulses per second. Examples on the micropollutants of this kind are carbamazepine, citalopram and furosemide.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.07.011.

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Publication V

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Nutrient recovery from wastewater through pilot scale electrodialysis

Nutrient recovery from wastewater through pilot scale electrodialysis

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ARTICLE INFO

ABSTRACT

Nutrient recovery performance utilising an electrodialysis (ED) process was quantified in a 30-cell pair pilot reactor with a 7.2 m^2 effective membrane area, utilising domestic anaerobic digester supernatant, which had been passed through a centrifuge as a feed source (centrate). A concentrated product (NH_4-N 7100 ± 300 mg/L and K 2490 ± 40 mg/L) could be achieved by concentrating nutrient ions from the centrate wastewater dilute feed stream to the product stream using the ED process. The average total current efficiency for all major cations over the experimental period was $76 \pm 2\%$ (NH_4-N transport 40%, K transport 14%). The electrode power consumption was 4.9 ± 1.5 kWh/kgN, averaged across the three replicate trials. This value is lower than competing technologies for NH_4-N removal and production, and far lower than previous ED lab trials, demonstrating the importance of pilot testing. No significant variation in starting flux densities and cell resistance voltage for subsequent replicate treatments indicated effective cleaning procedures and operational sustainability at treatment durations of several days. This study demonstrates that ED is an economically promising technology for the recovery of nutrients from wastewater.

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1. Introduction

The depletion of natural resources and increasing fertilizer prices due to either increased demand, energy costs or resource limitations has increased pressure to develop new processes for enhanced resource recovery (Xie et al., 2016). According to Batstone et al. (2015) and Mehta et al. (2016), a substantial fraction of global macronutrient requirements, such as PO_4-P, K and NH_4-N could be recovered from existing waste streams such as municipal wastewater treatment effluents.

Electrodialysis (ED) is an emerging electrochemical membrane process capable of concentrating and separating ions from wastewater (Zhang et al., 2009; Morantes et al., 2011; Thompson Brewster et al., 2016, 2017a). ED processes utilize an alternating series of cation exchange membranes (CEMs) and anion exchange membranes (AEMs), placed between the terminal anode and cathode. Applied current generates an internal potential gradient used to concentrate or dilute ions from an aqueous solution through ion migration (Thompson Brewster et al., 2016).

Traditional ED has been utilised in applications such as brackish water desalination, table salt production, and industrial process water demineralization (Strathmann, 2010). More recently, emergent ED applications aim to concentrate nutrients from waste streams (Ippersiel et al., 2012; Zhang et al., 2013; Ledezma et al., 2015), including prefermented hydrolysed sludge, (Tao et al., 2016). Laboratory scale ED has demonstrated the potential of nutrient recovery from wastewater sources. For example, Pronk et al. (2006) utilised laboratory scale ED to concentrate NH_4-N and PO_4-P by a factor of 3.2 (>14 000 mg/L NH_4-N, >600 mg/L PO_4-P) in continuous ED experiments with current efficiencies between 38 and 50%. Mondor et al. (2008) and Ippersiel et al. (2012) used electrodialysis to concentrate NH_4-N to 14.25 g/L and 21.35 g/L from swine manure with a batch ED process respectively. ED for NH_4-N and K recovery from domestic anaerobic digester supernatant (the liquid reject stream from centrifuges) is a relatively new application and the limits of nutrient concentration for this wastewater stream have not been evaluated thus far (Mehta et al., 2015; Thompson Brewster et al., 2017a) and the use of synthetic wastewaters does not achieve proof of concept for real wastewaters.

Previous laboratory scale experimental work has been undertaken utilising ED coupled with PO_4-P recovery, utilising a crystallization precipitation process (Wang et al., 2015; Tran et al.,

2014). For example: Wang et al. (2015) utilised ED for the simultaneous recovery of NH4-N and PO4-P from synthetic wastewater, coupled with a struvite reactor. Removal ratios of 96–100% for NH4-N and 86–94% for PO4-P were obtained with this integrated ED and struvite crystallization process. A similar integrated nutrient recovery approach to separate and recover phosphate as CaPO4 was investigated by Tran et al. (2014). Another benefit of coupled crystallization/ED nutrient recovery is a reduction in membrane scaling (Thompson Brewster et al., 2017a; Xie et al., 2016). Membrane scaling in ED increases the cell resistance, decreases ion migration and selectivity, and can eventually cause irreversible membrane scaling (Xie et al., 2016; Mikhaylin and Bazinet, 2016). According to Thompson Brewster et al. (2017a) the scaling of ED membranes in wastewater treatment can be reduced by more than 50% by applying struvite crystallization pre-treatment to the centrate. Although studies have demonstrated ED as a suitable technology for resource recovery from wastewater, no work has been reported in scientific literature at a larger pilot scale. This is critical, as power efficiency in particular is highly dependent on large numbers of internal cells to utilize current effectively, which requires larger ED systems.

A dominant aspect driving the practical feasibility of ED technologies is power consumption. Different NH4-N removal and recovery technologies have a large variation in energy requirements. Power consumption for the removal of NH4-N by conventional sludge based nitrification and denitrification treatment processes ranges from approximately 6.18–13.6 kWh/kg NH4-N treated (Xie et al., 2016; Maurer et al., 2003; Schaubroeck et al., 2015). The anammox treatment process is lower with estimates of 1.50–5.02 kWh/kg NH4-N treated (Schaubroeck et al., 2015). ED is more practical for nutrient removal at high concentrations than for full wastewater treatment, but recovered nitrogen is a valuable product, and nitrogen removal from centrate reduces overall plant load. The recovery and concentration of NH4-N by other technologies such as NH4-N stripping with air and acid absorption for (NH4)2SO4 production uses 25 kWh/Kg NH4-N (Maurer et al., 2003). Commercial N-production fixing NH3 from atmospheric nitrogen (Haber-Bosch process, dominant for nitrogen manufacturing) ranges from 10.3 kWh/kg utilising natural gas to 12.5 kWh/kg NH4-N using oil (Maurer et al., 2003). Energy consumption below 10 kWh/kg NH4-N is necessary for ED to compete as a potential alternative for the Haber-Bosch process (though recovery from wastewater also offsets treatment energy costs). The recovery of NH4-N by ED has been estimated to be 18.05 kWh/kg NH4-N by Ippersiel et al. (2012), well above the required threshold levels. The current work applies electrodialysis pilot scale to identify whether the process can economically compete with both existing nitrogen treatment technologies, and as an alternative for nitrogen production via the Haber Bosch process. This work will also quantify the maximum NH4-N product concentration achievable utilising the ED processes and aims to validate previous results (in lab) that struvite crystallization, as a pretreatment for ED can be a viable technology to control ED membrane scaling.

2. Methods

2.1. Centrate wastewater and struvite pre-treatment

Feed water for this experiment consisted of centrate at the Luggage Point Wastewater Treatment Plant (WWTP) (Brisbane, Australia). The chemical analysis of the feed water used in this experiment is shown in Table 1. The centrate was pre-treated by a struvite crystallizer system to precipitate phosphorus as struvite (MgNH4PO4. 6H2O). For struvite crystallization magnesium sulphate (MgSO4) was used as Mg source, dosed at a molar ratio of 1:1 (Mg:P) and sodium hydroxide (NaOH) to maintain pH at 8.5. The struvite crystallizer was operated onsite and 60% P removal was observed as shown in Table 1. Post-crystallised centrate (hereafter referred as ED dilute feed) was gravity fed from the overflow to a 200L dilute feed inlet tank for the ED cell system.

2.2. Pilot ED cell configuration

A 30-cell pair pilot scale ED unit was utilised for this experimental work, supplied by ABR Process Engineering (Brisbane, Australia). The effective internal membrane area was 0.4 m × 0.3 m (0.12 m^2 per membrane, 7.2 m^2 total system membrane area). Thickness of the spacers was 6 mm, the wider spacers were utilised to minimise clogging and fouling that may occur when treating centrate wastewater (Thompson Brewster et al., 2016). The unit was equipped with 31 CEM membranes (General Electric CR67) and 30 AEM membranes (General Electric AR204SZRA). CEM membranes were placed next to the cathode and anode chambers to minimise the transfer of chlorine ions into the electrode chambers. Ti/PtIrO2 electrodes (295 × 400 × 1.5 mm) were used as the anode and cathode (ABR Process Engineering). 200 L high-density polyethylene tanks were used for the one pass dilute feed, and recirculated electrolyte rinse solution and recirculated concentrate product stream. A 100 L high-density polyethylene tank was used to collect the post ED dilute stream from the ED cell for sampling purposes. The post ED dilute stream outlet tank then overflowed to a sewer drain. All reservoir tanks were covered, but were vented to maintain atmospheric pressure. A process logic controller (cRIO-9066 CompactRIO controller, National Instruments) and Lab View software (National Instruments 2015) was employed to control, operate and log operational data from the pilot ED cell system. Further detail of process logic controller and sensors utilised can be found in the supplementary material S1.

2.2.1. Operating conditions

Each of the three separate replicates operated over 72 h. Peristaltic pumps (Master Flex 24 V, 570 R.P.M. and Master Flex Easy Load II, L/S 36 pump head) used to transport the concentrate product and dilute feed streams at a flow rate of 1250 mL/min (75 L/h). Pre-treated centrate was used as initial concentrate. The initial volume of the concentrate product and electrolyte rinse solution recirculation loops was 47.5 L (25 L in reservoir and 22.5 L in ED cell)

Table 1
Average chemical analysis of pre struvite centrate feed water and post struvite ED dilute feed water over the 35 d experimental period (n = 9). Samples were taken directly from the struvite feed tank and ED dilute feed tank.

mg/L		K	Mg	Na	P	S	Cl-	Ca	NH4	COD
Centrate	Total	231 ± 77	23 ± 3	437 ± 100	162 ± 67	21 ± 4	719 ± 191	35 ± 6	847 ± 391	369 ± 183
	Soluble	228 ± 68	3 ± 01	426 ± 85	160 ± 65	19 ± 4	719 ± 191	34 ± 4	847 ± 391	316 ± 44
ED dilute feed	Total	232 ± 41	1 ± 2	1003 ± 333	58 ± 46	118 ± 12	768 ± 211	25 ± 4	835 ± 267	351 ± 124
	Soluble	232 ± 43	0.6 ± 1	975 ± 349	59 ± 55	115 ± 17	768 ± 211	25 ± 4	835 ± 267	314 ± 82

and 183 L respectively. Concentrate product and electrolyte rinse solutions recirculated continuously from the reservoir (multi-pass), while the feed was single pass. For each replicate, 5400L of dilute feed was treated over the 72 h. The return flow of the electrolyte rinse solution and concentrate product solutions provided mixing within the respective reservoirs. 0.05 M H_2SO_4 was used as electrolyte rinse solution with an initial electrical conductivity of 10 mS/cm². The conductivity of the electrolyte rinse solution was maintained at 10 mS/cm² during the experimental period by dosing 3.6 M H_2SO_4 solution from a reservoir using a peristaltic pump controlled by the PLC. A potentiostat (100 V, 100 A, Rectifiers Australia) was used to supply a constant current of 2.5 A (20 A/m²). The optimal current density was identified by undertaken limiting current density plots to determine a suitable current density (see section 2.5 and 3.1. The ED cell was cleaned with 60 L of 0.5% NaOCl solution and 60 L of 1% HCl solution after each replicate run. At the end of each replicate, the cell was drained and alkaline (NaOCl) cleaning solution was recirculating through the cell for approximately two hours. The cell was drained again after alkaline cleaning and flushed with water before acid cleaning to remove all residual alkaline cleaning solution from the system and prevent pH neutralization. In the acid cleaning stage a 1% HCl solution (initial pH 1) was recirculated through the cell overnight and the ED cell was drained after cleaning before starting the next replicate run.

2.3. Sampling and analysis

Sampling was undertaken 4 times during the 72-h experimental period, with one 50 mL sample aliquot taken from each of the four respective reservoirs. Sample aliquots were collected at time intervals of 0, 24, 48 and 72 h. Electrolyte rinse solution, concentrate product and dilute feed sample aliquots were collected from the reservoir bulk solution, and the post ED cell dilute stream sample was collected directly from ED cell outlet pipe. All samples were analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer Optima 7300DV, Waltham, MA, USA) after nitric acid digestion for total and soluble cation concentrations (Ca, Na, K, Mg) and Lachat QuickChem flow injection analysis (FIA) (Lachat Instruments, Loveland, CO, USA) for soluble NH_4^+-N, PO_4^{3-}-P, NO_x-N and NO_2^--N. The start (0 h) and finish (72 h) samples were also analysed by: ion chromatography (IC) for anions (Dionex ICS-2100 IC system, Dionex, CA, USA); gas chromatography for volatile fatty acids (VFA) (Agilent Technologies 7890A GC System, CA, USA); and chemical oxygen demand (COD) (Merck Spectroquant® COD cell tests HC565173 25–1500 mg/L Spectroquant®). Suspended solids (TSS) were determined as per standard methods (A.P.H.A., 1985). Total solution volumes for the concentrate product and electrolyte rinse solution were measured over the experimental period by ultrasonic level sensors (Echopod DL10 Ocean controls, Flowline Australia).

2.4. Current – voltage curve

Limiting current density trials were undertaken to determine the ohmic region and associated current for the optimal operation of the ED cell. The limiting current density (i_{lim}) was established by plotting the slope of the current density (A m⁻²) against the cell resistance (V). The Initial limiting current trial was undertaken up to the 100 V maximum of the potentiostat. To determine the ohmic region, the voltage on the potentiostat was increased in 500 mA increments to the maximum output voltage of 100 V while maintaining the amperage chronoamperometrically across the ED cell. The experimental duration of each tested current density was 1.5 hydraulic retention times (27 min HRT) of the ED cell. Post struvite centrate feed water was utilised in all current - voltage experiments

and was used for both the dilute feed and concentrate product streams. The fluids were not recirculated; it was a single pass operation at a flow rate of 1.25 L/h during this experimental period. Electrolyte rinse solution was fed at the same flow rate as the dilute feed and concentrate product. The electrolyte rinse solution was also discarded once it had passed through the ED cell maintaining standardised electrical conductivity conditions. To determine the final i_{lim} the two slopes belonging to the ohmic and the plateau region were plotted and the bisection point determined (Kroll et al., 1999).

2.5. Molar ionic flux density

The molar ionic flux density (J_i) across the cation exchange membranes was determined for NH_4-N, Na, K and Mg at the 24, 48 and 72 h experimental times by the molar concentration in the feed minus the molar concentration of the dilute stream out, divided by total effective membrane area (3.6 m²).

2.6. Current efficiency

Current efficiency (CE) is defined as the ratio of moles transferred of the target cation with time compared to the faradays of electricity passed through the ED cell. Equation (1) was used to determine the theoretical molar transport capacity.

$$TC(theoretical) = \frac{NtI}{FV} \tag{1}$$

where TC (theoretical) is the theoretical transport capacity, N is the number of cell pairs stacked in the ED cell, t is the duration of the experiment (s), I is the average current density (A/m²), F is the Faraday constant (96486 C/mol) and V is the volume of the cell (L).

The measured transport is determined using equation (2).

$$TC\ (measured) = \sum n_i z_i \tag{2}$$

where the TC (measured) is the measured transport from the experiment, n_i is the moles of species i per L and z_i is the valency of the species i. The overall CE is the measured transport capacity over the theoretical transport capacity. The species i consisted of the major cations K, Mg, Na, Ca and NH_4-N.

3. Results

3.1. Limiting current density

Fig. 1 shows the current density-voltage results for the pilot scale ED unit operated in the range of 0.8 and 4 mA/cm². A linear increment in voltage was observed as the current density increased from 0.8 to 3.2 mA/cm², identified as ohmic region on Fig. 2. Above 3.2 mA/cm², a sharp decline in slope was observed suggesting increased resistance due to concentration polarization or depletion of ions in the membrane boundary layer. This region was identified as a plateau region as shown in Fig. 2. Based on the slopes of the ohmic and the plateau regions, 3.2 mA/cm² was estimated as a limiting current density (i_{lim}) for the given operating conditions and reactor type. The pilot scale ED reactor was operated at 2 mA/cm² for all other experimental work, as 60–80% of the ohmic region prior to the limiting current density region is considered as ideal current density (Strathmann, 2004). Higher current densities were not possible due to the 100 V limitation of the potentiostat used to operate the pilot ED cell system and therefore the water splitting region of the over limiting current density was not reached (Strathmann, 2010).
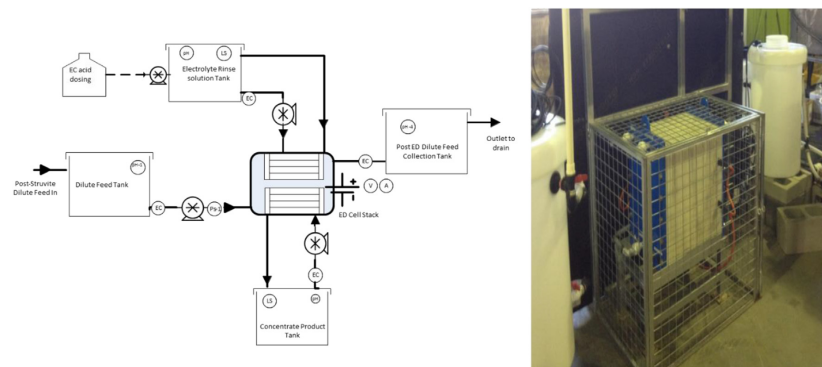
Fig. 1. Schematic drawing of pilot ED cell and associated dilute feed, concentrate product electrolyte rinse solution and post ED cell dilute stream tanks. Electrical conductivity (EC), pH (pH), pressure transducer (PS), amperage (A)/voltage (V) transducers and ultrasonic level sensors (LS) are shown.
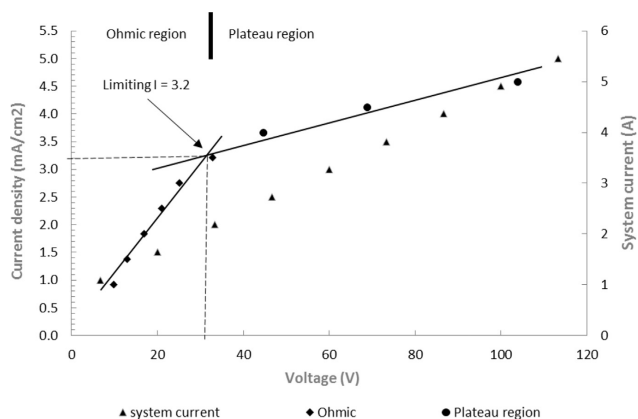

Fig. 2. Current-voltage plot showing the system current (A), limiting current density (i_{lim}) (mA/cm^2) and the presence of the ohmic and plateau regions. The limiting current density was determined by the intersection of the two slopes belonging to the ohmic and the plateau regions.

3.2. Concentration factor, EC and ED cell parameters

The electrical conductivity of the ED dilute feed reduced from 8.3 ± 0.1 mS/cm^2 to 6.4 ± 0.1 mS/cm^2 (23% reduction) over the single pass (95% confidence interval, n = 3). A total of 5400 L of feed in total was treated. The initial electrical conductivity of the concentrate product was 7.7 ± 0.6 mS/cm^2 and this increased to the final electrical conductivity of 59 ± 4 mS/cm^2 (Fig. 3). The average total amount of undiluted 18 M H_2SO_4, used to maintain the electrolyte rinse solution EC over the experimental period was 470 ± 20 mL. This was sufficient to maintain the electrolyte rinse solution EC above 10 mS/cm^2 over the experimental duration.

For all three replicates, cation concentrations increased over the experimental period of 72 h. The maximum concentration of NH$_4$-N and K achieved was 7100 ± 800 mg/L and 2500 ± 100 mg/L, respectively. However, the rate of accumulation for all major cations started to decrease after 24 h and had plateaued at the 72-h experimental duration. Fig. 4 shows the concentrations for Na, NH$_4$-N, K and PO$_4$-P over the experimental duration. Fig. 5 shows the accumulated mass of concentrated cations over the experimental duration.

The ICP, FIA, IC, total COD (COD$_{tot}$) and soluble COD (COD$_{sol}$) results for the concentrate stream is shown in Table 2.

The mean pH for the ED dilute feed was 8.75 ± 0.04, while the concentrate product stream pH was 8.7–8.9 for the first 12 h, then dropped to 8.4–8.6 for the remaining 48 h. Concentrate product pH data is provided in Supplementary material 3. The pH of the post ED cell dilute stream leaving the ED cell also decreased over the experimental duration. The final VFA concentrations achieved in the concentrate at the end of the experimental period were <10 mg/L for acetic acid, butyric acid, valeric acid, hexanoic acid and butanol, respectively. The final total suspended solids in the concentrate were 0.7 ± 0.3 mg/L.
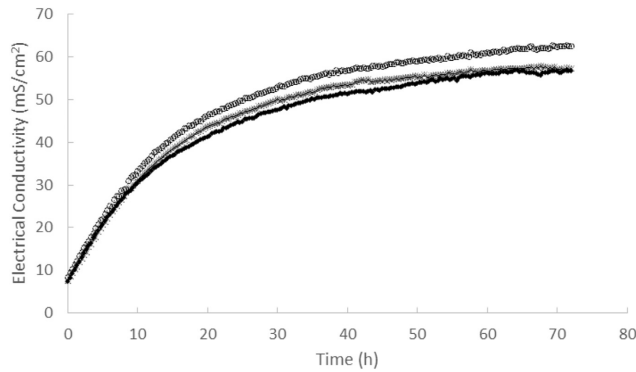
Fig. 3. Electrical conductivity of the three-concentrate product replicates over the experimental duration.
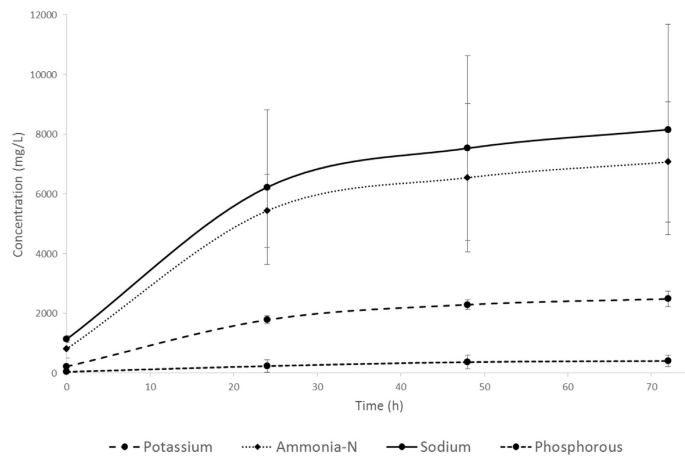

Fig. 4. Concentration of major cations in the concentrate product over the experimental duration ((n = 3) Error bars = 95% confidence interval).

3.3. ED cell voltage

Fig. 6 shows the time-series voltage for the ED cell for each replicate. Voltage initially increased, likely due to process polarization (Kroll et al., 1999). Following this, potential reduced to a stable 20–30 V over the remainder of the experimental period. The average current efficiency calculated at the start of the experimental period was $78 \pm 7\%$ and reduced to $64 \pm 16\%$ at the end of the 72-h experimental period.

3.4. ED cell ionic flux density and current efficiency

The overall average ionic flux density for the major ions in mol/m^2h was 0.3 ± 0.2 (NH$_4$), 0.17 ± 0.14 (Na), 0.0004 ± 0.00018 (Mg), 0.03 ± 0.012 (K), 0.003 ± 0.0031 (Ca) 0.006 ± 0.0019 (PO$_4$) and 0.004 ± 0.0061 (SO$_4$). Fig. 7 shows the ionic flux density (J_i, mol/m^2h) for the 24, 48 and 72-h individual sampling periods over the experimental period. The flux density of all major cations appeared to decrease over the experimental period, but further statistical analysis indicated no significant time trend (p > 0.05). This was by correlated analysis of variance (ANCOVA) using the anovan command in Matlab (time as continuous variable, replicate # as categorical variable). Only phosphorous had a p of less than 0.1 (p = 0.08) for time, and all others were greater than 0.25. The overall removal rates for the major cations was 23%, 21%, 19%, 8%, 19%, 17% and 5% for NH$_4$, Ca, K, Mg, Na, P and SO$_4$, respectively.

The experimental average total current efficiency for the experimental period was $76 \pm 2\%$ (NH$_4$-N transport 40%, K transport 14%). The initial total current efficiency was 78 ± 7 and decreased to $64 \pm 16\%$ over the 72-h experimental duration. This represents a 14% decrease in total current transport efficiency over the experimental period.
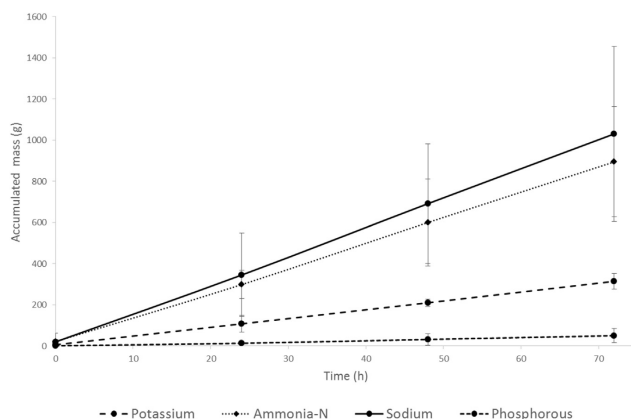
Fig. 5. Accumulated mass of major cations in the concentrate product over the experimental duration ((n = 3) Error bars = 95% confidence interval).

Table 2
Proximate chemical analysis for the concentrate stream at the end of the experimental period (n = 3, error bars = 95% confidence interval).

mg/L	K	Mg	Na	P	S	Cl-	Ca	NH$_4$	COD
Total	2486 ± 258	1 ± 0.1	8105 ± 3518	408 ± 296	1150 ± 186	7788 ± 1173	24 ± 77	7069 ± 2022	934 ± 360
Soluble	2466 ± 198	0.34 ± 0.1	8106 ± 3438	408 ± 291	1145 ± 2186	7788 ± 1173	24.24 ± 76	7069 ± 2022	852 ± 463
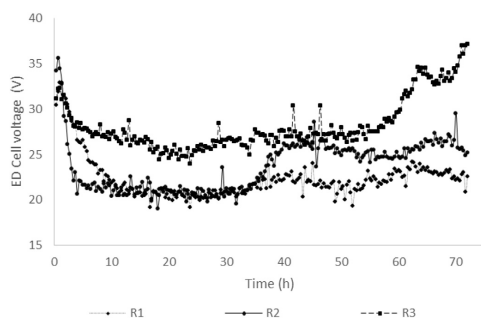
Fig. 6. Individual replicate time series ED cell voltages during the experiment.

3.5. Concentrate volume

ED cell inlet pressure for both the dilute feed stream and the concentrate product stream remained stable and did not increase over the experimental duration. Inlet pressure data from the concentrated product and dilute feed stream are shown in the supplementary material S1. The initial average volume of the concentrate product stream reservoir was 27L with concentrate volume increasing to 128 ± 3 L at the end of the 72-h experimental period due to osmotic flux. Fig. 8 shows the increase in product volume over the experimental duration.

4. Discussion

The results demonstrate that a concentrated product (suitable as fertilizer) could be achieved by concentrating nutrient ions from the dilute feed stream to the concentrate product stream via the ED process. The main negative in this application is the relatively high Na concentrations, which could be reduced through modified struvite precipitation (which uses MgOH rather than NaOH to raise pH). This elimination would reduce Na levels down to (on the order of 2000 mg/L) which would make it suitable for use as liquid fertilizer in many applications, but NH$_4^+$ and K$^+$ could be further separated and concentrated through processes such as stripping, for NH$_4^+$ or adsorption (NH$_4^+$ and K$^+$) (Hedström, 2001; Guo et al., 2018).

It is noted that osmotic flux was constant, while molar flux (and conductivity reduction) reduced during the experiments. A reduction in the ionic molar flux and removal efficiency at high product concentrations has been previously reported. Rottiers et al. (2014) identified back diffusion of ions from the concentrate to dilute stream due to a concentration gradient as a major limiting factor for ion concentration and efficiency in ED processes, and the type of membranes only marginally influenced this. Thompson Brewster et al. (2017b) suggested that limitations to high product concentrations may be due to increased back diffusion due to large concentration gradients, and osmotic and electro-osmotic water fluxes. Mondor et al. (2008) reported the NH$_4$-N concentration was partly limited by osmosis and the transfer of solvated ions from the dilute feed stream to the concentrate product stream, and as the concentrate ionic strength increases, solvated ion water transport decreases current efficiency and limits concentration extent. This indicates an optimal operational period in batch mode, and that in continuous mode, a concentrate flush stream is needed, to avoid excessive product ionic strength (and conductivity).

A decrease in ionic molar flux density and transfer efficiency has also been highlighted by Mondor et al. (2009) where they identified membrane fouling and scaling as a major factor reducing efficiency
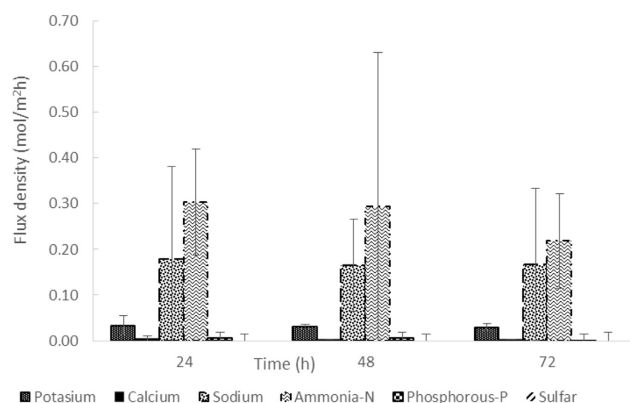
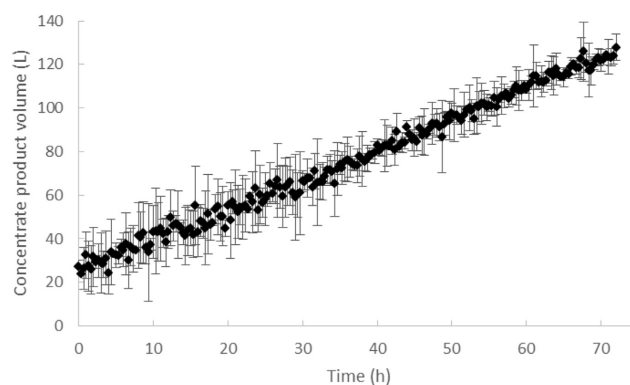Fig. 7. The ionic flux density (J_i, mol/m^{2}h) between the 24, 48 and 72-h individual sampling periods.

Fig. 8. Increase in concentrate product volume over the experimental duration (n = 3, error bars = 95% confidence interval).

of the ED process. Experimental results and modeling simulations by Thompson Brewster et al. (2017a) showed a significant reduction in precipitation formation when struvite pre-treatment was applied to centrate feed water prior to the ED system. A mass balance indicates a 29% loss of PO_4-P and a 92% loss of Ca from the concentrate product and electrolyte rinse solution. This loss of PO_4-P and Ca indicates that precipitates formed within the cell. The formation of these precipitants would have contributed to the increase in the voltage resistance across the ED cell. However, this voltage increase from the formation of precipitants is only temporary as the membrane flux densities clearly return to similar ranges after the cleaning process has been undertaken. The inlet pressure did not change substantially, indicating that flow pathways are not substantially restricted (supplementary material S1).

The overall mass balances for this experiment indicated a 28% total loss of NH_4-N over the experiment; a major part of this loss could be related to the volatilisation of NH_4-N to the atmosphere. This ammonia could be captured by pressurising the headspace, or recovering headspace gas through an acid bath. The alternative is to

acidify the concentrate (which may enhance cation recovery) or use a more concentrated acid as electrolyte. The average up-concentration (mg/L) of NH_4-N achieved in this experimental work was 8.77 times and recovery is $23 \pm 3\%$. This results compares to ranges reported by Zhang et al. (2013) and Ippersiel et al. (2012) who reported over 7 and 6.67 times NH_4-N up-concentration, respectively. These results are higher than results reported by Pronk et al. (2006) where an up-concentration factor of 3.2 times was reported. We note that $23 \pm 3\%$ is a relatively low recovery compared with biological alternatives such as Anammox, but that; (a) the cost of this removal is relatively low (see comparative analysis below); (b) a higher reduction can be achieved with longer retention times or multiple passes, albeit at an increased cell potential due to decreased conductivity; and (c) related to this, a higher recovery will be achieved on more concentrated streams, where electrodialysis becomes increasingly competitive.

Water flux from the dilute to the concentrate was substantial, with product volume increasing from 25 L to 125 L. This large increase in concentrate product volume is due to the water transport

caused by osmosis and electro-osmosis (solvation shells of water molecules transporting through membrane together with ions) (Pronk et al., 2006). Robbins et al. (1996) and Rottiers et al. (2014) also identified the water flux through the ED membranes as a major obstacle when ED is used as a concentration technology. According to Rottiers et al. (2014), the water flux by electro-osmosis in ED is far higher than by osmosis. This is normal, and the time stability of osmotic flux (with increasing concentration in product) indicates that the flux is mainly electro-osmotic, and not the main reason for the plateauing in cation fluxes (which is likely more related to back diffusion). Water flux could be decreased by utilising concentrate product as electrolyte, which would reduce the osmotic gradient between the product and the electrolyte. However, the electro-osmotic transfer and the associated volume increase in the concentrate product can actually be beneficial. Harvesting could be achieved by removing further concentrate product once a specific volume and concentration had been reached. This would enable continuous operation of the cell and would eliminate the need for batch-wise replacement of concentrate.

The power consumption over the three replicates was 4.9 ± 1.5 kWh/kg NH_4-N. This does not include pumping energy, which is fairly high in a pilot unit (~5 kWh/kg NH_4-N) due to the use of peristaltic pumps, but given the relatively low diluent side pressure drop, averaging 0.3 bar (see supplementary info), full-scale pumping energy would be an order of magnitude lower than the electrochemical energy input (on the order of 0.1 kWh/m^3, Batstone et al., 2015). In any case, energy consumption is at the lower end of the reported energy requirement of $6.18-13.6$ kWh/kg NH_4-N utilising current wastewater treatment technology (activated sludge and aeration for nitrification) (Xie et al., 2016; Maurer et al., 2003; Schaubroeck et al., 2015). Compared with side-stream anammox, ED is a competitive process, achieving an equivalent energy consumption, but with lower footprint (HRT 0.3 h), simpler in operation (single stage process), and without the difficulty in inhibition or start-up, where there is difficulty in obtaining seed sludge. In addition, it recovers the nitrogen, rather than destroying it. However, ED is dependent on a relatively high solution electrical conductivity, and as ions are recovered, electrical conductivity drops. This limits the recovery (in this case, 23% NH_4-N per pass), as well as placing a limit on ultimate recovery, with increased voltage required at lower ammonia concentrations. It is likely that anammox will be a more effective technology at lower ammonia concentrations (<1000 mgN L^{-1}), with ED becoming progressively more competitive above 1500 mgN L^{-1}.

When the calculated energy consumption reported in this study is compared with other NH_4-N recovery technologies, for example NH_4-N stripping with air and $(NH_4)_2SO_4$ and the commercial Haber-Bosch process for N-fertilizer production, it is (excluding pumping) below 50% of the energy requirements per kg of NH_4-N reported for current technologies. This result demonstrates the ED process as a more energy efficient NH_4-N recovery option, and while it does not produce a highly concentrated product (e.g., $(NH_4)_2SO_4$ it is possible to directly use the product as liquid fertilizers. The energy consumption for electrodialysis is acceptable, and given the relatively low pressure drop, pumping energy can be relatively low. Higher conductivity feeds (i.e., more concentrated) would further decrease energy consumption, and improved membranes may provide additional efficiency gains, but the essential feasibility is established.

Key areas of future research include optimising removal extent and product recovery, determining performance under longer term operation, eliminating sodium and unwanted anions like chloride, and further optimising energy consumption.

5. Conclusion

Development of a low-cost technology to recover nitrogen from wastewater is crucial for economic and environmental benefit. The feasibility of pilot scale electrodialysis (ED) for nutrient concentration and recovery from municipal wastewater was studied in this work. The maximum achievable total NH_4-N concentration measured experimentally was approximately 7100 ± 800 g/L, which corresponded to a concentration factor of approximately 8 times. Mean current efficiency for ion transport was $76 \pm 2\%$. The power consumption 4.9 ± 1.5 kWh kg NH_4-N, is well under previous results and estimates for nutrient recovery by ED. This makes the process economically competitive for nitrogen removal by advanced reactive technologies such as anammox, and advantageous for nitrogen production vs manufacturing by the Haber-Bosch process.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.02.021.

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Publication VI

Kimmo Arola, Andrew Ward, Mika Mänttäri, Mari Kallioinen, and Damien Batstone
Transport of pharmaceuticals during electrodialysis treatment of wastewater

Transport of pharmaceuticals during electrodialysis treatment of wastewater

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ABSTRACT

Electrodialysis (ED) is a promising emerging electrochemical membrane technology for nutrient concentration and recovery from wastewater. However associated environmental safety aspects have to be assessed before utilizing concentrated nutrient produced by ED, for instance as fertilizer. Municipal wastewaters contain various micropollutants that have the potential of being concentrated during the ED treatment processes. This study quantified the transport of pharmaceuticals during ED nutrient recovery from synthetic centrate wastewater. Specifically, it is evaluated whether pharmaceutical micropollutants are mobile, and therefore able to transport across the cation exchange membranes and concentrate into the ED concentrate product. Results demonstrate that NH_4^+-N, PO_4^{3-}-P and K^+ could be concentrated up to 5 times in the concentrated ED product (3700—4000 mg/L NH_4^+-N, 21—25 mg/L PO_4^{3-}-P, 990—1040 mg/L K^+). Target micropollutants, such as diclofenac, carbamazepine and furosemide were largely retained in the diluent, with less than 8% being transported across to the concentrate product (feed micropollutant concentration 10 or 100 μg/L) based on the final target pharmaceutical amounts in the ED concentrate product (μg). Some transport of micropollutants such as atenolol, metoprolol and hydrochlorothiazide was observed to the concentrate product. For instance a final concentration of 10.3, 9.4 and 8.6 μg/L on average was measured for these pollutants in the final ED concentrate product (final volume ~1 L) in experiments with a feed water (initial volume 20 L) containing only 10 μg/L of target pharmaceuticals. Transport of pharmaceuticals across the ED membranes was concluded to be dominated mainly by the molecule hydrophobicity/hydrophilicity as well as electrostatic interactions between pharmaceutical molecules and ED membranes. Particularly excluded were those having a negative charge and high hydrophobicity such as diclofenac and ibuprofen.

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1. Introduction

Fertilizer prices are increasing globally due to increased demand, increased energy costs, and resource limitations such as depleting phosphorus reserves (Batstone et al., 2015; FAO, 2017; Mehta et al., 2015). This has increased focus on enhanced nutrient recovery. A substantial fraction of macronutrients such as phosphorus, potassium and nitrogen (100% P and K, 50% N) could be recovered from existing waste streams such as agricultural and municipal wastewater effluents (Batstone et al., 2015; Mehta et al., 2016). Electrodialysis (ED) is an emerging electrochemical membrane process, where anions and cations are migrating through cation exchange membranes (CEMs) and anion exchange membranes (AEMs) due to electrical current, which is generated by applying potential to the terminal electrodes (Baker, 2004).

Zhang et al. (2009) studied the utilization of ED for the separation of nutrient ions and organic compounds from salts in synthetic reverse osmosis (RO) concentrate. Nitrate (NO_3^-) and phosphate ions ($H_2PO_4^-$ and HPO_4^{2-}) could be readily removed from the synthetic RO concentrate, removal rates of 92% for NO_3^- and 86% for the phosphate ions was achieved, separation of monovalent ions such as NO_3^- could be further enhanced to 98% by using monovalent selective membrane. Although the separation of nutrients from the organic fraction of the RO concentrate was possible, the separation of salts from nutrient ions was difficult as salts were transported together with the nutrient ions. ED was used by Wang et al. (2015) for the simultaneous recovery of ammonium and phosphorus from synthetic wastewater simulating side

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streams of anaerobic digestion by coupling ED with a struvite reactor. Removal ratios of 96—100% for ammonia salt and 86—94% for phosphate could be reached by integrated process of ED and struvite crystallization. Zhang et al. (2013) used similar approach to separate and recover phosphate from industrial anaerobic effluent of potato processing wastewater. Zhang et al. (2013) reached over 7 times increase in the concentrate phosphate concentration (from 0.93 to 6.64 mmol/L).

Ward et al. (2018) demonstrated pilot scale nutrient recovery performance utilizing an ED process containing a 30-cell pair ED. This pilot study utilized domestic anaerobic digester supernatant, which had been passed through a centrifuge and a struvite crystallization process, as a feed source (centrate). A concentrated product (NH_4—N 7100 $\pm$ 300 mg/L and K 2490 $\pm$ 40 mg/L) could be achieved by concentrating nutrient ions from the centrate wastewater dilute feed stream to the concentrate product stream using the ED process. The electrode power consumption was 4.9 $\pm$ 1.5 kWh/kgN, averaged across the three replicate trials. This value is lower than competing technologies for NH_4—N removal and production, and far lower than previous ED lab trials, and demonstrates practical economic and commercial viability of the technology.

Although ED have proven to be a promising technology for the resource recovery from wastewaters, it is also important that the valuable resources recovered with ED do not cause any risks for the environment. The various waste streams of municipal wastewater treatment may contain significant amounts of micropollutants, which may hinder the utilization of fertilizer products obtained by emerging technologies such as ED. According to Falås et al. (2016), many micropollutants are biologically recalcitrant to wastewater treatment processes and thus are not readily degraded during treatment. According to Gao et al. (2016), Zhu and Chen (2014) and Arola et al. (2017) the concentrations of micropollutants such as carbamazepine, caffeine and diclofenac can vary significantly depending on the waste streams, concentration ranges from 0.05 to 5 μg/L up to 0.1—100 μg/L being reported in the waste streams of municipal wastewater treatment. Thus, it is important to identify whether micropollutants can migrate through the ED membranes or accumulate in the concentrate product.

Limited studies have been conducted related to the removal of pharmaceuticals utilizing ED in wastewater treatment applications (Banasiak et al., 2011; Pronk et al., 2006; Vanoppen et al., 2015). Pronk et al. (2006) evaluated ethinylestradiol, diclofenac, carbamazepine, propranolol and ibuprofen from urine by continuous laboratory scale ED. These were preferentially retained in the feed stream (>95% retained by ED membranes) and hence excluded from concentrate product. For analytical reasons the target micropollutants were spiked in the urine at concentrations up to 10 μM (>2 mg/L), at levels well above normal sewage. Ethinylestradiol was completely retained by ED membranes over the whole experimental period of 90 days. Retentions for other pollutants were very high initially (≥95% for first 10—20 days), but some breakthrough especially for propranolol and ibuprofen occurred during extended operation (90 days). The main retention mechanisms for these micropollutants were identified to be membrane adsorption/partitioning and diffusion (Pronk et al., 2006).

Banasiak et al. (2011) studied the sorption of pesticide endosulfan and the hormone estrone by ED membranes. Sorption was studied by treating a background solution (5 g/L NaCl and 84 mg/L of $NaHCO_3$), containing 2.5 mg/L of each pollutant, in a continuous laboratory scale ED (dilute feed and concentrate recirculated to one feed reservoir). 67% of the endosulfan and 42% estrone (596 and 381 μg/cm^3) was adsorbed to the ED membranes during 14 h ED experiments with a neutral feed solution (pH 7). At an increased pH of 11, the sorption decreased to 47 and 31% for endosulfan and

estrone potentially due to competitive sorption between degraded/dissociated endosulfan and estrone and the ion-exchange membranes. Whilst a significant amount of pesticide endosulfan and estrone hormone could be rejected from the concentrate product with ED, an accidental release of these adsorbed pollutants from the membranes for instance during membrane cleaning would result in environmental aquatic discharge (Banasiak et al., 2011).

Vanoppen et al., (2015) studied the transport of trace organic contaminants such as carbamazepine, diclofenac, ketoprofen and metoprolol through ED membranes in saline water matrix (10 or 100 g/L NaCl). It was concluded that the transport of organic contaminants like carbamazepine, diclofenac and metoprolol (<20% transport through ED membranes in most cases) was mainly result of electrostatic interactions and overall the transport was mainly driven by diffusion. For uncharged contaminants the diffusion driven by concentration difference, together with the affinity for the membrane were the main drivers for the transport of the target contaminants whereas the molecule size was less significant.

Due to very limited studies on the fate of micropollutants in the ED processes, especially with feed solutions containing ambient concentrations of pollutants, and with domestic wastewater (rather than urine), this study aims to better evaluate the fate of micropollutants through the ED process. Thus, this study aims to examine if pharmaceuticals can migrate across the ion exchange membranes to the concentrated product during short-term ED experiments (8 h) with synthetic wastewater and to identify the determining factors for possible transfer of pharmaceuticals. If the transport of pharmaceuticals to the concentrate product can be minimized or prevented completely, the utilization of the concentrate product for fertilizer applications becomes more feasible.

2. Materials and methods

2.1. ED unit configuration and operating procedure

Experiments were performed in a batch-mode with a laboratory scale ED unit supplied by ABR Process Engineering (Brisbane, Australia), with electrolyte rinse solution (initial volume 10.0 L), product (hereafter named as concentrate product, initial volume 0.6—0.65 L) and dilute feed (initial volume 19.6—19.65 L) being recirculated through reservoirs. The ED unit was equipped with five CEMs (General Electric CR67) and four AEMs (General Electric AR204SZRA), each with an effective area of 10 × 15 cm (150 cm^2), and a 4 mm spacing. The ED membranes had the following characteristics (CEM and AEM): membrane thickness 0.6 mm and 0.5 mm, ion exchange capacity 2.1 and 2.4 meq/g, pH stability 0.5—12 and 0.5—10.5 and resistance (0.01N NaCl) of 10 and 7 Ω/cm^2 (data from the manufacturer). The anode and cathode were Ir MMO mesh coated with titanium (ABR Process Development, Brisbane, Australia). The configuration of the ED unit consisted of 4.5 cell pairs, an anode chamber, a cathode chamber, four product chambers and four dilute feed chambers (Fig. 1). An additional cation exchange membrane was fitted to the cathode chamber to prevent the migration of chloride ions into the electrolyte rinse solution.

The dilute feed, electrolyte rinse solution and concentrate product reservoirs were ventilated to maintain atmospheric pressure. A potentiostat (Manson model HC3104) was used to supply a constant current of 0.5 A (33.3 A/m^2). The 0.5 A current used was in a similar ranges utilized by Thompson Brewster et al. (2017a), Wang et al. (2015), Zhang et al. (2009) and Zhang et al. (2013) in laboratory scale ED experiments. The concentrate product and dilute feed stream had a constant flow rate of 23 mL/min each and they were recirculated back to their respective reservoirs during ED experiments. Sulfuric acid (H_2SO_4, 1.5 mL/L) was used as electrolyte rinse solution and was supplied to the anodic and cathodic
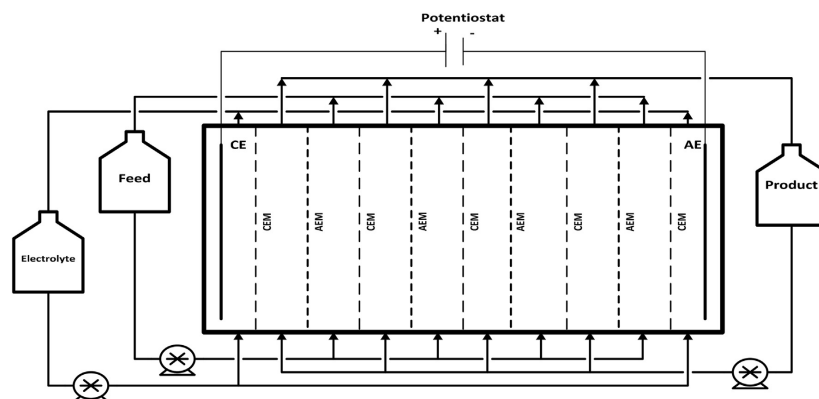
Fig. 1. Schematic diagram of the used ED setup.

compartments at the same flowrate of 23 mL/min and was recirculated back to the electrolyte rinse solution reservoir during ED experiments. The conductivity of the electrolyte rinse solution was maintained by between 10 and 15 mS/cm during ED experiments by dosing 0.3–0.5 mL/L H_2SO_4 to the reservoir when conductivity decreased below 10 mS/cm.

Synthetic wastewater (pH 8.5) having a similar composition of NH_4^+, Na^+ and K^+ as post-crystallized centrate (supernatant from the centrifugation of anaerobic digestate after struvite crystallization) was used in ED experiments as a dilute feed (Table 1, Thompson Brewster et al., 2017a and Ward et al., 2018). Duration of each experiment was 8 h and 10 µg/L (treatment 1) and 100 µg/L (treatment 2) micropollutant dilute feed concentrations were tested to determine the effect of micropollutant concentration in the dilute feed to the micropollutant transport across the membrane. Triplicate 8 h experiments were conducted, and a stronger initial concentrate product solution treatment was also tested (5510 mg/L NH_4^+, 6317 mg/L Na^+, 1513 mg/L K^+, 44.4 mg/L Ca^{2+}, 26.5 mg/L PO_4^{3-}-P, treatment 3). This was done to study the effect of osmotic water transport on the migration of target pollutants across the ED membranes. As the product concentration overall increases the osmotic transport of water will change, which may influence the transport of target compounds, and relative proportioning for migration may change. The ED cell was cleaned with 0.5% HCl solution (3 h cleaning) after each experiment. Samples (dilute feed, feed out, electrolyte rinse solution and concentrate product) were taken at the beginning and at the end of each experiment. Sample volumes were 1.5 mL for the micropollutant analyses (taken directly to glass HPLC vials) and 50 mL for other analyses (taken to 50 mL plastic sample containers). 1.5 mL micropollutant samples were kept in the freezer before analysis and 50 mL samples were kept at 4 °C after sampling before analysis.

Table 1
Average properties of synthetic wastewater used as dilute feed stream in ED experiments.

Parameter	Concentration, mg/L	Added as
NH_4^+-N	756 (738–784)	NH_4Cl, $NH_4H_2PO_4$
Na^+	933 (912–982)	$NaHCO_3$, NaCl, NaOH
K^+	196 (192–203)	K_2SO_4
Ca^{2+}	4.6 (4.5–4.8)	$CaCl_2·2H_2O$
PO_4^{3-}-P	4.8 (4.4–5.2)	$NH_4H_2PO_4$

2.2. Desorption study

The potential adsorption of micropollutants to the ED membranes was studied in a separate 24 h desorption experiment, where methanol-water (50/50) desorption solution containing 45 g/L NaCl was used to desorb the pharmaceuticals from the ED membranes after extended 24 h ED experiment with a target pharmaceutical concentration of 100 µg/L. Methanol and NaCl have been utilized for the desorption purposes before to desorb micropollutants such as diclofenac from adsorption membrane and ion exchange resins (He et al., 2017; Laundry and Boyer, 2013). According to Laundry and Boyer (2013) the combination of methanol and NaCl provides efficient desorption ability especially for diclofenac, since the NaCl provides counter ions for the ion exchange as a form of Cl^- ions and the interactions with a less polar solvent methanol enables the desorption. For diclofenac both are required to reverse the sorption process (Laundry and Boyer, 2013). Thus, combined solution of methanol and NaCl was chosen as desorption solution. The ED cell was rinsed after the experiment with Milli-Q water for 30 min before desorption experiments. The desorption solution was then recirculated through the ED cell for 24 h after the rinsing and solution was sampled at 2- and 24-h period of desorption.

2.3. Target micropollutants

Target micropollutants were chosen based on the widespread presence in the effluents of anaerobic and aerobic municipal wastewater treatment (Gao et al., 2016; Zhu and Chen, 2014; Arola et al., 2017). Micropollutants used comprised of atenolol, caffeine, carbamazepine, diclofenac, furosemide, hydrochlorothiazide, ibuprofen, metoprolol and trimethoprim (Table 2). Most of these nine pollutants are unreadily removed in traditional municipal wastewater treatment processes (Falås et al., 2016; Arola et al., 2017). Samples for the micropollutant analyses were taken directly from the dilute feed, electrolyte rinse solution and concentrate product reservoirs and post ED dilute samples were taken directly from the post ED dilute line, since the post ED dilute stream was also recirculating back to the dilute feed reservoir.

Table 2 presents also the acid dissociation constants pKa, which describe the acidity of a specific molecule. If pKa value of a pollutant

Table 2
Molecular characteristics of the studied micropollutants and their concentrations in the ED dilute feed stream (pH 8.5).

Micropollutant	Classification	Formula	Molar mass, g/mol	pKa, -	log K_{ow}, -	Charge at pH 8.5	Feed concentration, µg/L
Ibuprofen	Pain killer	$C_{13}H_{18}O_2$	206.3[a]	4.9[a]	4.0[a]	negative	10.5 (9.4–12.4) 103 (94–123)
Diclofenac	Non-steroidal anti-inflammatory drug	$C_{14}H_{11}Cl_2NO_2$	296.2[a]	4.2[a]	4.5[a]	negative	11.3 (9.8–12.1) 108 (103–113)
Carbamazepine	Anti-epileptic agent and mood stabilizer	$C_{15}H_{12}N_2O$	236.3[a]	13.9[a]	2.5[a]	positive	12.2 (9.7–13.8) 107 (89–128)
Atenolol	Cardioselective beta blocker	$C_{14}H_{22}N_2O_3$	266.3[a]	9.6[a, b]	0.16[a, b]	positive	10.1 (9.7–10.6) 124 (91–166)
Metoprolol	Selective beta blocker	$C_{15}H_{25}NO_3$	267.4[a]	9.7[b]	1.9[a, b]	positive	10.4 (9.6–10.9) 99 (90–109)
Furosemide	Loop diuretic	$C_{12}H_{11}ClN_2O_5S$	330.7[a]	3.8[a]	2.0[a]	negative	11.0 (10.6–11.3) 108 (98–119)
Hydrochlorothiazide	Thiazide diuretic	$C_7H_8ClN_3O_4S_2$	297.7[a]	7.9[a]	−0.07[a]	negative	11.7 (10.7–13.5) 116 (103–147)
Trimethoprim	Antibiotic	$C_{14}H_{18}N_4O_3$	290.3[a]	7.1[a]	0.91[a]	negative	10.0 (9.0–10.5) 100 (84–116)
Caffeine	Central nervous system stimulant	$C_8H_{10}N_4O_2$	194.2[a]	14.0[a]	−0.07[a]	positive	10.5 (10.2–11.0) 102 (97–105)

Data obtained from.
[a] PubChem, 2017.
[b] Maurer et al. (2007).

is lower than the pH of wastewater it is considered to be dissociated and negatively charged (Sui et al., 2010; Thomas and Foster, 2005). Log K_{ow} describes the hydrophobicity/hydrophilicity of a substance. If log K_{ow} value is higher than 3.2 the substance is considered to be clearly hydrophobic and might have higher tendency to adsorb into membrane structure if hydrophobic (Tadkaew et al., 2011; Sui et al., 2010; Hai et al., 2011).

2.4. Analytical techniques

Elemental analysis was performed from the 50 mL samples by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (PerkinElmer Optima 7300DV, Waltham, MA, USA) for total cation concentrations (calcium, sodium, potassium, magnesium). Lachat QuickChem8500 Flow Injection Analysis (FIA) (Lachat Instruments, Loveland, CO, USA) was used to measure NH_4^+-N, PO_4^{3-}-P, NO_x-N and NO_2^--N. During each experiment the pH and conductivity of all solutions was measured with TDS Aqua-CPA (ISO 9001:2008) pH and conductivity meter (k = 10 sensor). Total solution volumes were also measured at the start and end of the experimental period (dilute feed, concentrate product and electrolyte rinse solution volumes in the reservoirs).

Target micropollutants studied in this work were analyzed by ultra-fast liquid chromatography (UFLC) coupled with mass spectrometry (MS). A volume of 20 µL of sample was injected in a Shimadzu UFLC connected to an AB Sciex 4000QTrap QLIT-MS equipped with a Turbo Spray source. The UFLC instrument was equipped with a 5 µm, 250 × 4.6 mm Altima C18 column (Grace), which was operated at 40 °C. Each sample was analyzed separately in both positive and negative ion multiple reaction monitoring (MRM) mode. In positive mode the eluent A was 95% acetonitrile/ 5% HPLC grade water (v/v) and eluent B was 1% acetonitrile/99% HPLC grade water (v/v); both containing 0.1% formic acid. The flow rate was 1 mL/min and the elution gradient started with 15% of eluent A, increasing to 100% in 12.5 min and held isocratically for 2.5 min. The eluent returned then to initial conditions in 0.2 min and the column was re-equilibrated for 6 min leading to a total time of 21.2 min. In negative mode the eluent A was 50% acetonitrile/50% methanol (v/v) and eluent B was HPLC grade water. The flow rate was 1 mL/min and the elution gradient started with 15% of eluent A, increasing to 90% in 7 min and held isocratically for 3 min before rising to 100% in 2 min and held isocratically for 5 min. Then the

eluent returned to initial conditions in 2 min and the column was re-equilibrated for 5 min leading to a total time of 24 min. Two transitions were monitored in the MRM mode. The first transition was used for quantification and the second one for confirmation purposes only. The quantification was performed using 8 points external calibration curves obtained from the injection of standard solutions ranging from 0.1 to 100 µg/L. Linear or quadratic regression was used depending on the compound, which gave good fits with R2 values above 0.99.

2.5. Molar ionic flux and current efficiency

The molar ionic flux (J_i) across the cation exchange membranes was determined for NH_4^+-N, Na^+, K^+ and Ca^{2+} at 1 and 8 h of ED operation from a mass balance by using equation (1).

$$Ji = \frac{Q2 * C2 - Q1 * C1}{A} \tag{1}$$

where C1 is the concentration (mol/L) of respective cation in the post ED dilute stream (flow out from the ED cell) and C2 is the concentration (mol/L) of respective cation in the dilute feed (feed into the ED cell), Q1 is the flow rate out of the ED cell (L/h), Q2 is the flow rate to the ED cell (L/h) and A is the total cation exchange membrane area (m^2).

Current efficiency (CE) is defined as the ratio of moles transferred of the target cation with time compared to the faradays of electricity passed through the ED cell. Equation (2) was used to determine the theoretical molar transport capacity.

$$TC(theoretical) = \frac{NtI}{FV} \tag{2}$$

where TC (theoretical) is the theoretical transport capacity, N is the number of cell pairs stacked in the ED cell, t is the duration of the experiment (s), I is the average current density (A/m^2), F is the Faraday constant (96486 C/mol) and V is the volume of the cell (L).

The measured transport is determined using equation (3).

$$TC\ (measured) = \sum n_i z_i \tag{3}$$

where the TC (measured) is the measured transport from the

experiment, n_i is the moles of species i per L and z_i is the valency of the species i. The overall CE is the measured transport capacity over the theoretical transport capacity. The species i consisted of the major cations K^+, Na^+, Ca^{2+} and NH_4^+-N.

2.6. Analysis of variance (ANOVA) on ionic flux

Analysis of variance (ANOVA) was done to determine if flux was impacted by treatment (10 μg/L, 100 μg/L, 100 μg/L strong product), categorical factor with three levels — treatment 1, 2, 3, or time (1 h vs 8 h), also effectively categorical. ANOVA was done using the anovan command in Matlab R2018b. Interactions were checked, but were never significant, and not used for the main model. A 5% significance threshold was applied, and p-values reported for significant effects.

3. Results and discussion

3.1. Ionic flux, efficiency and concentration of nutrient ions

The ionic flux of the major cations that migrated from the dilute feed to the concentrate product compartments was estimated by equation (1). Highest overall ionic fluxes (J_i, mol.m^{2}h) for the major cations, being 0.43 ± 0.06, 0.31 ± 0.07, 0.05 ± 0.007 and 0.001 ± 0.0002 mol/m^{2}h for NH_4^+-N, Na^+, K^+ and Ca^{2+}, and 0.001 ± 0.0001 mol/m^{2}h for PO_4^{3-}-P were obtained in the ED treatment 1 (10 μg/L pollutant concentration). Fig. 2 shows the average ionic fluxes (J_i, mol/m^{2}h) for the 1 and 8-h operating periods in all ED experiments with a dilute feed micropollutant concentrations of 10 and 100 μg/L (treatment 1 and 2) as well as in the experiments with strong initial product (treatment 3). Small decrease in the ionic fluxes (0–19%) was observed overall over the experimental period for all major ions, mainly in treatment 1 and 2. ANOVA indicated that treatment was always a significant factor (mainly with treatment 3) with p-values of $0.02–1 \times 10^{-5}$ (Table SI1). Time was significant (causing a decrease in ionic flux) for K^+ (p = 0.001) and NH_4^+ (p = 0.01). The largest decrease in the average ionic molar flux (mol/m^{2}h) was 19% for the anion PO_4^{3-}-P in the ED treatment 1 (t-test p = 0.025). This decrease can be expected as the product EC

becomes higher the transfer of ions decreases by back-diffusion. Precipitation as calcium phosphates is unlikely, as Ca^{2+} and PO_4^{3-} was very small in the feed (4.6–4.8 mg/L, Table 1), and calculated solublity indices were generally an order of magnitude lower than for published precipitation indices ($CaHPO_4$, $Ca_3(PO_4)_2.xH_2O$ (Musvoto et al., 2000). More likely the partial depletion of phosphate in the feed water during the ED treatment (17.5, 19.1 and 14.2% depletion of PO_4^{3-}–P on average in the treatment 1–3) decreases the phosphate flux.

The total current efficiency for the transfer of all cations (K^+, Na^+, Ca^{2+} and NH_4^+-N) across the CEM membranes was calculated by equations (2) and (3). The average total current efficiency for the experimental period was $66 \pm 1\%$ (NH_4^+-N transport 57%, K^+ transport 6%) in the treatment 1 (10 μg/L pollutant concentration), $63 \pm 2\%$ (NH_4^+-N transport 58%, K^+ transport 6%) in the treatment 2 (100 μg/L pollutant concentration) and $57.8 \pm 0.2\%$ (NH_4^+-N transport 58%, K^+ transport 6%) in the treatment 3 (100 μg/L pollutant concentration, strong initial product). The initial total current efficiencies were between 57.9 and 66.7% on average and decreased to 57.6–64.8% over the 8-h experimental duration. These values were lower than reported by Ward et al. (2018) for pilot scale ED, who reported average total current efficiency of $76 \pm 2\%$ (NH_4–N transport 40%, K transport 14%) for all major cations over the experimental period. A concentration factor of 5 ± 0.5 was achieved in the ED experiments with the dilute feed (treatment 1 and 2) for the nutrient ions NH_4^+-N, PO_4^{3-}-P, K^+ and Ca^{2+} (Table 3). For instance for the NH_4^+-N the initial concentration was around 750–770 mg/L in the initial feed (treatment 1 and 2, feed volume 19.6–19.65 L) and around 3700–4000 mg/L in the final concentrate product (final product volume 1.0–1.1 L, initial product volume 0.60–0.65 L, 2% transport extent). Thus, around 26% of the ammonia present in the initial feed was removed and the feed conductivity decreased from the initial 10.3–10.5 mS/cm to the 7.8–8.7 mS/cm by the end of the experiments (average conductivity removal around 21%).

A reduction in the ionic molar flux at high product concentrations has been previously reported (Ward et al., 2018). Rottiers et al. (2014) identified back diffusion of ions from the concentrate to dilute stream due to a concentration gradient as a major limiting factor for ion concentration and efficiency in ED processes, and the
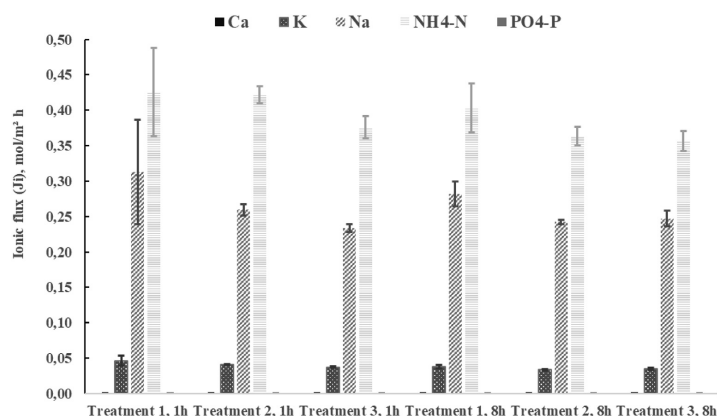

Fig. 2. Average ionic fluxes (J_i, mol/m^{2}h) for the 1 and 8-h operating periods in the triplicate ED experiments with a dilute feed micropollutant concentrations of 10 (treatment 1) and 100 μg/L (treatment 2) as well as in the experiments with strong initial product (treatment 3). ED operated 8 h at constant current density of 33.3 A/m^2 and constant flow rate of 23 mL/min (n = 3, error bars = 95% confidence interval).

Table 3
Average concentrations of NH_4^+-N, PO_4^{3-}-P, K^+ and Ca^{2+} in the ED dilute feed and final concentrate products as well as their concentration factors during ED experiments. ED operated 8 h at constant current density of 33.3 A/m^2 and constant flow rate of 23 mL/min (n = 3).

		Treatment 1 (10 µg/L)	Treatment 2 (100 µg/L)	Treatment 3 (100 µg/L with strong initial product)
Feed concentration, mg/L	NH_4^+-N	747	768	5510
	PO_4^{3-}-P	5.1	4.6	27
	K^+	198	193	1513
	Ca^{2+}	4.6	4.5	44
Final concentration in product, mg/L	NH_4^+-N	3692	3957	5723
	PO_4^{3-}-P	25	21	27
	K^+	1038	987	1587
	Ca^{2+}	22	22	44
Concentration factor, -	NH_4^+-N	4.9	5.2	1.0
	PO_4^{3-}-P	4.9	4.5	1.0
	K^+	5.2	5.1	1.0
	Ca^{2+}	4.7	4.8	1.0

type of membranes only marginally influenced this. Thompson Brewster et al. (2017b) suggested that limitations to high product concentrations might be due to increased back diffusion due to large concentration gradients, and osmotic and electro-osmotic water fluxes. Mondor et al. (2008) reported the NH_4^+-N concentration was partly limited by osmosis and the transfer of solvated ions from the dilute feed stream to the concentrate product stream, and as the concentrate ionic strength increases, solvated ion water transport limits the concentration extent. This finding was also supported by Ward et al. (2018).

A NH_4^+-N ion concentration factor of 5 achieved in this study was quite low when compared to the 8.77 reported by Ward et al. (2018) in the pilot scale electrodialysis. Although Ward et al. (2018) utilized the same membranes used in this experimental work, the volume ratios utilized by Ward et al. (2018) were different, which explained the difference. Results obtained by Ward et al. (2018) for the current density vs voltage when operated in the range of 0.8 and 4 mA/cm^2 showed a linear increment in voltage, as the current density increased from 0.8 to 3.2 mA/cm^2, the ohmic region was identified. A sharp decline in slope was then observed suggesting increased resistance due to concentration polarization or depletion of ions in the boundary layer of membrane. Based on the slopes of the ohmic and the plateau regions, the 33A/m^2 used in this work was 60% higher than Ward et al. (2018) and would have fallen into the concentration polarization area of the plot, therefore the water splitting region or the over limiting current density was reached (Strathmann, 2010). Due to this the obtained average ionic flux were high when compared to ones reported by Ward et al. (2018) in the treatment of centrate wastewater with a pilot scale ED. High ionic fluxes were also expected, since the ED experiments were conducted at laboratory scale with a simple water matrix, which did not contain impurities able to foul the membranes, like in real wastewaters. Organic impurities present in the real wastewaters can also interact with cations via ion-pairing, activity changes, and other interactions (Stumm and Morgan, 1996), which will have an effect to the ionic fluxes. The operation of the ED cell in the limiting current density area would have also resulted in lower current efficiencies (58–66% in this study compared to 76% reported by Ward et al. (2018)) due to current being used to split water on the membranes.

3.2. Transport of pharmaceuticals during ED

Transport of target micropollutants, all being pharmaceuticals, through the ion exchange membranes to the final ED concentrate product during ED experiments are illustrated in Figs. 3 and 4. Ion exchange membranes excluded (<0.6% pollutant transport, Table 4) diclofenac, ibuprofen, furosemide as well as carbamazepine and caffeine efficiently from the concentrate product in the ED treatment 1, total amount of these pollutants being below 1.2 µg (corresponding to concentrations <1.22 µg/L) in the final concentrate product with a nutrient concentration factor of 5 (Fig. 3). Similar trend was observed in the ED treatment 2 and 3 (Fig. 4). However, the transport of other pollutants atenolol, metoprolol, hydrochlorothiazide and trimethoprim to the final concentrate product was more intense during ED experiments (0.4–7.4% pollutant transport, Table 4). The results indicates that atenolol and metoprolol are either accumulating to the final concentrate product (pollutant concentration µg/L higher in product than in the initial feed) or proportioning (pollutant splits between product and diluent compartments according to hydraulic changes including osmotic transfer to concentrate) whereas trimethoprim and hydrochlorothiazide are proportioning and other pollutants are retained (rejected by the membranes in comparison with water). The concentrations of target micropollutants in the feed and final concentrate products over different ED treatments are presented in the supplementary information (Table SI2).

Overall, less than 8% from the pollutants present in the dilute feed solutions was transported to the final concentrate product in the ED treatments conducted (Table 4). Thus, over 92% retention of all target pollutants, calculated as a percentage of the feed micropollutant amount (µg) retained by the ion exchange membranes, was achieved in the ED experiments.

On average the atenolol, metoprolol, hydrochlorothiazide and trimethoprim (Figs. 3 and 4, Table 4) had the highest tendency to move across the ion exchange membranes to the concentrate product. Out of these pollutants the atenolol and metoprolol were both positively charged and also relatively hydrophilic (Table 2), especially in the case of atenolol (log K_{ow} value 0.16). Hydrochlorothiazide and trimethoprim were negatively charged at the feed pH of 8.5, but both are hydrophilic (log K_{ow} −0.07 and 0.91). Diclofenac, ibuprofen, furosemide and carbamazepine were all retained efficiently in the ED experiments by ion exchange membranes (Figs. 3 and 4, Table 4). Diclofenac, ibuprofen and furosemide were all negatively charged and especially diclofenac and ibuprofen were very hydrophobic (Table 4), whereas the carbamazepine was positively charged at pH 8.5, but had relatively high log K_{ow} value (2.5). Thus, based on these results the hydrophobicity/hydrophilicity had a strong influence on the micropollutant transport through the ED membranes, but also charge had some influence on the transport. The result that some transport of both positively and negatively charged pollutants occurred (transport both across the anion and cation exchange membranes) during ED experiments highlighted the influence of molecule hydrophobicity/hydrophilicity to the micropollutant transport.

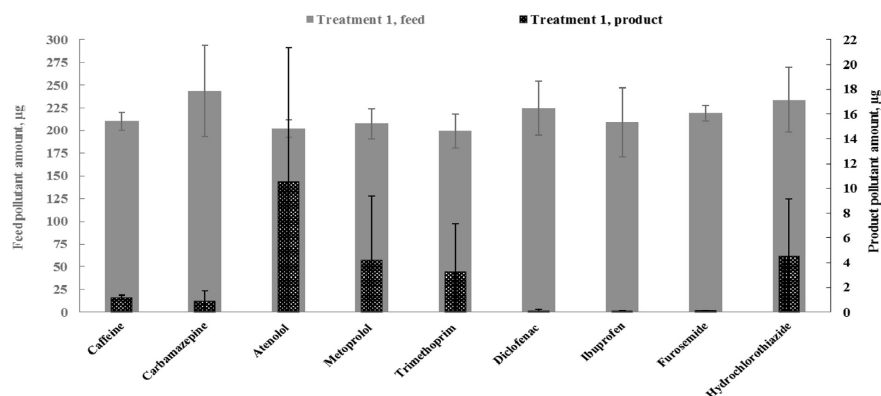Pronk et al. (2006) studied the removal of micropollutants from

Fig. 3. Average amount (µg) of target micropollutants in the dilute feed (left vertical axis, grey data series) and final concentrate product (right vertical axis, black patterned data series) in the ED treatment 1 (target micropollutant concentration of 10 µg/L). (n = 3, error bars = 95% confidence interval).
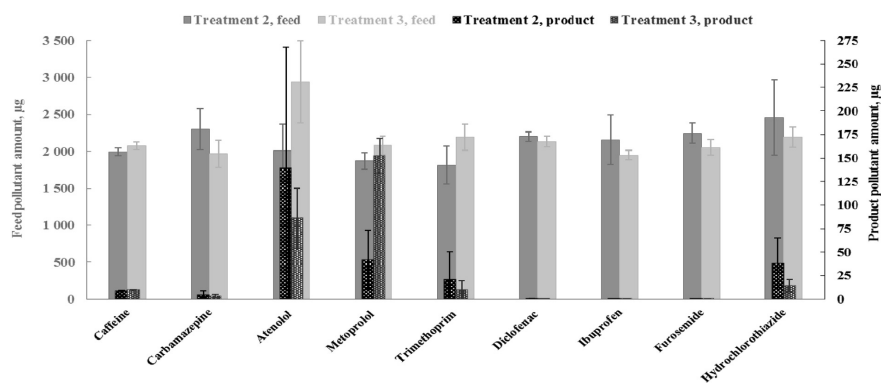

Fig. 4. Average amount (µg) of target micropollutants in the dilute feed (left vertical axis, dark grey (treatment 2) and light grey (treatment 3) data series) and final concentrate product (right vertical axis, black patterned (treatment 2) and dark grey patterned (treatment 3) data series) in the ED treatment 2 (micropollutant concentration of 100 µg/L) and 3 (micropollutant concentration of 100 µg/L, strong initial product). (n = 3, error bars = 95% confidence interval).

Table 4
Average percentage of the target pollutants transported from the dilute feed solution to the final concentrate product in the 8 h ED treatments. (n = 3, 95% confidence interval given in brackets).

	Percentage of pollutant in the final concentrate product from the initial feed								
Treatment	Caffeine	Carbamazepine	Atenolol	Metoprolol	Trimethoprim	Diclofenac	Ibuprofen	Furosemide	Hydrochlorothiazide
1 (10 µg/L)	0.57% (0.08)	0.32% (0.33)	5.3% (5.6)	2.0% (2.4)	1.6% (1.9)	0.04% (0.05)	0.04% (0.006)	0.06% (0.003)	1.9% (2.2)
2 (100 µg/L)	0.45% (0.03)	0.22% (0.21)	6.5% (5.2)	2.2% (1.7)	1.2% (1.8)	0.01% (0.01)	0.004% (0.0007)	0.0059% (0.0001)	1.7% (1.3)
3 (100 µg/L + strong initial product)	0.49% (0.03)	0.17% (0.08)	2.9% (0.9)	7.4% (1.1)	0.4% (0.4)	0.00053% (0.0006)	0.004% (0.008)	0.009% (0.006)	0.7% (0.3)

anthropogenic urine with ED and concluded that the removal of micropollutants with ED was determined by a combination of adsorption (effected highly by molecule hydrophobicity/hydrophilicity), diffusion, sieving and electrostatic interactions. However, unlikely as observed by Pronk et al. (2006), the sieving and

diffusion did not have such a strong role in the micropollutant removal with ED based on the results and micropollutant properties (Figs. 3 and 4, Tables 2 and 4). No clear effect of pollutant molecule size to the micropollutant transport was noticed and the initial micropollutant concentration did not have a significant effect

on the micropollutant transport through the ion exchange membranes (Figs. 3 and 4, Table 4). Thus, the micropollutant transport through the ion exchange membranes was dominated by other factors, such as adsorption, hydrophobicity/hydrophilicity and electrostatic interactions. Pronk et al. (2006) also estimated that the long-term operation of ED without significant permeation of micropollutants to the concentrate product is possible, if the micropollutant concentrations in the feed are close to environmental concentrations. Based on this study this is true for most of the target pollutants studied, however some permeation of micropollutants such as atenolol and metoprolol were observed already within 8 h ED operating time even though the dilute feed micropollutant concentration was only 10 μg/L (Table 4).

When considering the utilization of final concentrate product for fertilizer application the final concentration of few pollutants, being atenolol (10.3 μg/L), metoprolol (9.4 μg/L), hydrochlorothiazide (8.6 μg/L) and trimethoprim (9.8 μg/L), in the concentrate product was significant in ED treatment 1, when considering the threshold values 0.1 and 0.01 μg/L for pharmaceuticals in surface waters set by US food and drug administration and European medicine agency (Besse and Garric, 2008). However, the actual concentration of these pollutants in the real anaerobic wastewater treatment plant effluents would be expected to be an order of magnitude lower (Gao et al., 2016, Zhu and Chen, 2014) and dose of concentrate would be relatively low in comparison with irrigation water. Further treatment of the concentrate product might still be required before utilization, if wastewater was treated with ED then resultant concentrate product might contain significant amount of these pollutants. Although due to the highly concentrated nature of the concentrate product large dilutions would be required for application as a fertilizer, significantly reducing the concentration of ammonia and micropollutants for application purposes.

3.3. Adsorption of micropollutants

Mass balances calculated for target pharmaceuticals indicated that either adsorption or degradation of some pharmaceuticals occurred during short term ED experiments. The micropollutant amount for metoprolol, trimethoprim, diclofenac and furosemide was on average 6–17% lower at the end of 8 h ED experiments compared to the initial amount in the dilute feed. Adsorption to the ED membranes was major reason for pharmaceutical mass loss for pollutants atenolol, metoprolol and furosemide in the extended 24 h ED experiment, since the missing amount of these pollutants was completely desorbed to the desorption solution after 24 h desorption time (Table 5). A 2 h desorption time was able to desorb almost completely these pollutants from the ED membranes. For the trimethoprim and diclofenac potentially, some minor degradation occurred also during ED experiments, since only limited desorption occurred during desorption period (Table 5). Limited desorption for diclofenac was unexpected based on the excellent results (complete desorption) obtained by Laundry and Boyer

(2013) in desorption of diclofenac from anion exchange membranes.

Banasiak et al. (2011), who studied the removal of endosulfan with ED, identified losses to equipment, volatilization and degradation during the ED treatment or desorption as potential reason for micropollutant mass loss in addition to possible adsorption. However, losses to the ED equipment can be minimized by using glass and stainless-steel equipment and sample vials instead of polymeric material such as polystyrene (Banasiak et al., 2011). Micropollutant endosulfan losses to the equipment was not significant in the study made by Banasiak et al. (2011). Volatilization of micropollutants from aqueous media depends on the water solubility and volatility of the substances. Thus, small amounts of volatilization during ED can be possible for pollutants with high volatility (Banasiak et al., 2011). Therefore, potentially small part of the trimethoprim and diclofenac was either degraded during ED or potentially even slightly volatilized. However major part was presumably very strongly adsorbed to the ED membranes and could not be desorbed with the used solution and desorption time of 24 h.

Pronk et al. (2006) concluded an adsorption to the ED membranes as one of the major removal mechanisms of micropollutants when anthropogenic urine was treated with ED. In their study, the tendency of adsorption increased in the following order: carbamazepine, ibuprofen, propranolol and diclofenac. Electrostatic interactions and especially hydrophobicity was identified to have a major role in the adsorption behavior. Diclofenac was observed to adsorb the most to the ED membranes, potentially due to high hydrophobicity (Pronk et al., 2006). Similar observation about the factors effecting adsorption could be done in this study, since the beta blockers atenolol and metoprolol (adsorption mainly due to electrostatic interactions) as well as anti-inflammatory drug diclofenac (adsorption mainly due to hydrophobicity) had a clear tendency for adsorption, whereas the carbamazepine and ibuprofen did not show pronounced tendency for adsorption. Pronk et al. (2006) also studied desorption of micropollutants from ED membranes after long term experiments (90 days) by current reversal as well as by incubating ED membranes in a specific scintillation-counter cocktail to release the micropollutants from membranes. Current reversal was concluded to be slow and inefficient desorption method; only 34% of the adsorption could be released from the membranes after 840 h of current reversal. After an incubation period of 1000 h a total of 93% of the adsorbed micropollutants had been released from the membrane (Pronk et al., 2006).

Desorption of micropollutants from ED membranes can thus be a slow process and complete desorption might be challenging to achieve. According to the results of this study and findings from the literature (Pronk et al., 2006) especially hydrophobic pollutants such as diclofenac can adsorb strongly to the ED membranes. The adsorption of diclofenac could not be distinguished between AEM and CEM membranes with the arrangement of the desorption study.

Table 5
Percentage pollutant mass loss in the 24 h ED experiment with a pollutant concentration of 100 μg/L and in the 24 h desorption experiment as well as desorption efficiencies.

Mass balance	Percentage pollutant mass loss, %				
	Atenolol	Metoprolol	Trimethoprim	Diclofenac	Furosemide
Initial vs after 24 h ED experiment	42	52	51	37	29
Initial vs 2 h desorption	12	17	47	35	0
Initial vs 24 h desorption	−3	−6	48	35	−7
Desorption efficiency	**Recovered mass from total adsorbed mass, %**				
2 h desorption	71	68	7	6	102
24 h desorption	108	111	5	6	125

4. Conclusions

The transport of pharmaceuticals during ED treatment of wastewater was studied in this work. The aim was to examine the pharmaceuticals ability to transport across the ion exchange membranes and eventually concentrate into the concentrate product.

Laboratory scale ED was able to concentrate nutrients such as NH_4^+-N, PO_4^{3-}-P and K^+ up to 5 times (3700–4000 mg/L NH_4^+-N, 21–25 mg/L PO_4^{3-}-P, 990–1040 mg/L K^+). Less than 8% of the pollutants present in the dilute feed solutions were transported to the final concentrate product in the ED treatments conducted in this study. For many target pollutants, such as diclofenac, carbamazepine, furosemide, ibuprofen and caffeine, the transport extent was less than 1%. However, a small accumulation of atenolol and metoprolol as well as proportioning of micropollutants trimethoprim and hydrochlorothiazide was observed during ED experiments. These pollutants however are often present in an order of magnitude lower concentrations in the real wastewaters, and the ED concentrate product would be diluted before potential utilization as fertilizer. Thus, this study indicates that the ED can produce safe concentrate product for use as a fertilizer, which contains non-effective concentrations of studied micropollutants.

Transport of pharmaceuticals across the ED membranes depended largely on molecule hydrophobicity/hydrophilicity but also on electrostatic interactions between pharmaceutical molecules and ED membranes. Target pollutants having a negative charge at present pH conditions and high hydrophobicity such as diclofenac and ibuprofen were preferentially retained in the diluent. Further work with real wastewaters is required to confirm the observations of this study and to examine if ED can also retain other micropollutants to enable production of a concentrate product suitable for fertilizer purposes.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2019.06.031.

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