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STUDIES ON MEMBRANE SEPARATION FOR A COMBINED MEMBRANE AND BIOFILTRATION OF PESTICIDES IN GROUNDWATER BASED DRINKING WATER TREATMENT

BY
MAHDI NIKBAKHT FINI

DISSERTATION SUBMITTED 2019

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Studies on membrane separation for a combined membrane and biofiltration of pesticides in groundwater based drinking water treatment

PHD THESIS

by

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Curriculum Vitae

Mahdi is a Membrane Process Engineer with a special focus on Microfiltration (MF), nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO). He is currently a Ph.D. researcher at Aalborg University involved in MEM2BIO project working on pesticides removal from groundwater in Denmark using membrane technology.

Education:

2016-2019	Ph.D. in Chemical Engineering, Aalborg University, Denmark
2010-2013	M.Sc. in Chemical Engineering, Separation Processes, University of Tehran, Iran
2004-2009	B.Sc. in Chemical Engineering, Iran University of Science and Technology, Iran

Professional Experience:

2014-2016	Process Engineer, Haami Project Engineering Consultants, Tehran, Iran
2011-2013	Research Assistant, Multicomponent Separation Laboratory, University of Tehran
2008-2010	Research Assistant, Research Center for Membrane Separation Processes, IUST

English summary

Use of pesticides has immensely influenced the production of agriculture products and has probably saved millions from starvation, but it also exposes risk to the human's health as it may cause irritation of the eyes and skin and more severely nervous system disorders, reproductive problems, and cancer. In particular, contamination of slow generating drinking water resources such as groundwater aquifers is of great concern as it might cause a long-lasting exposure of the population to toxic pesticides. In Denmark, pesticides and their degradation products were detected in 21.8% of the drinking water wells, and the permitted value of 0.1 µg/L was exceeded in 4.3% of the cases in 2017. Existing simple drinking water treatment process consisting of aeration followed by sand filtration has been found to be insufficient for treatment of groundwater polluted by pesticides, and it is a necessity to introduce new treatment concepts to the drinking water production. This thesis is a part of a novel concept introduced by MEM2BIO project in which membrane filtration in combination with biological degradation is studied for the treatment of groundwater polluted by pesticides in Denmark.

Biofiltration with pesticides degrader bacteria has been previously shown to be capable of pesticides abatement in lab-scale but, suffers from the low concentration of micropollutants, and other nutrients in the water, therefore, the microbial community faces starvation and loses its density in long-term filtration. On the other hand, membrane filtration, which is also an effective method for the removal of pesticides produces a concentrated undesired residual retentate. If the membrane filtration concentrated retentate will be used as a feed for biological treatment, it might boost degradation potential and ensure the survival of degrader microbes. The study of this hypothesis is carried out by MEM2BIO project, which is a novel combination of membrane filtration with biodegradation. As the first work package of the MEM2BIO project, this thesis studied different membrane processes for pesticides removal from Danish groundwater and provided concentrated feeds for biodegradation.

In NF/RO studies, four commercial membranes were tested to treat groundwater polluted with three pesticides and pesticide transformation product (PTP), namely BAM, MCPA, and MCPP. It was found that NF membranes were not applicable for removal of pesticides while RO and LPRO membranes both could reject membranes at high levels. However, it was observed that NF membranes might be effective in micropollutant level concentration for phenoxy acid herbicides, MCPA and MCPP, as they bear negative charges and could be repelled by negatively charged NF membranes. Therefore, the concentration of pollutants might influence differently the membrane filtration depending on the properties of both membranes and pesticides and consequently, the separation mechanism of pesticides removal. The separation mechanism was found not to be governed only by steric hindrance, as the pore flow

model could not predict the rejection properly due to the presence of charged pesticides among the compounds. Both ionic environment and high recovery showed a similar effect on the rejection of pesticides from real groundwater matrix obtained from three locations in Denmark. The use of groundwater matrix with higher ionic strength stimulated pore-blocking effect resulting in elevated rejection values, but accelerating the membrane fouling and thus the flux decline. The XLE membrane was finally selected as the proper candidate to be used for pesticides removal with rejecting all the target pesticides >92% and having relatively a moderate permeate flux.

The XLE membrane was used to produce concentrated retentates for biodegradation step at different recoveries (50%, 80%, 90%). Although due to the ionic adsorption, the concentration of ions was not as high as expected, the concentration was sufficiently and distinctly high to be able to investigate the impact of membrane retentate on the biodegradation potential. The batch and lab-scale biodegradation experiments illustrated an improved biodegradation capacity when the retentates used, and the best removal and mineralization of BAM was observed from the retentate obtained from 90% recovery. The column experiments also showed that the concentrated feed led to complete and continuous removal of BAM for 40 days.

The use of aquaporin FO membranes in different FO systems from a very tiny setup and a prevalent lab-scale system to a hollow fiber pilot-scale setup revealed that the obtained results from the tiny equipment could be translated to pilot-scale rejection values. This can promote the use of FO process in different application with a simple, quick, and inexpensive method. The diffusion-based aquaporin FO membrane demonstrated an excellent rejection of >98% for all the pesticides while having a superior permeation flux compared to other few commercial FO membranes.

In scaling analysis studies between RO and FO processes, the threshold concentration of a model scalant, gypsum, in the feed water found to be higher for FO process when the same membrane was used in a similar setup to record flux decline as a result of scaling. Therefore, it can be concluded that the flux in the FO process is influenced by scaling to a lesser extent. The used membrane was a polydopamine incorporated TFC membrane that was successfully synthesized. The membrane showed high pesticides rejection values in both RO and FO (>91%) and permeate flux of ~34 LMH was obtained in the FO process.

The overall conclusion from this thesis is that the combination of RO membrane filtration with biological degradation is a promising way of treating pesticide-polluted groundwater. Investigations show that retentate from membrane filtration can boost the biodegradation of pesticides, and complete removal of pesticides can be achieved through this combined concept. The possibility of scaling-up and long-term performance of this hybrid treatment concept is currently being studied through a pilot plant located in a site on a contaminated drinking water well to be run for six months.

Dansk resume

Brug af pesticider har haft en kæmpe indflydelse på produktionen af landbrugsprodukter og har formentlig reddet millioner af mennesker fra at sulte. Men brug af pesticider udgør også en risiko for menneskers helbred, da de kan forårsage irritation af øjne og hud og mere alvorligt forårsage forstyrrelser på nervesystemet, evnen til forplantning og kræft. Forurening af drikkevandsressourcer så som grundvandsreservoir er specielt i fokus, da det kan forårsage langvarig udsættelse af befolkninger overfor giftige pesticider. I Danmark bliver pesticider og deres nedbrydningsprodukter fundet i 21,8% af drikkevandsboringerne, og den tilladte grænseværdi på 0,1 µg/L blev overskredet i 4,3% af fundene i 2017. Den nuværende ”simple drikkevandsrensning” bestående af beluftning efterfult af filtrering i sandfilter har vist sig ikke at være effektiv overfor grundvand forurenet med pesticider. Dermed er udvikling og anvendelse af nye teknologiske rensningskoncepter i drikkevandsproduktionen nødvendig. Studierne afrapporteret i denne afhandling er udført som et led i udviklingen af et nyt koncept i regi af MEM2BIO projektet, hvor membranfiltrering i kombination med biologisk rensning bliver undersøgt som rensningsmetode overfor dansk grundvand forurenet med pesticider.

Biologisk filtrering og rensning med specifikke pesticidnedbrydende bakterier har tidligere vist at være effektive i forhold til at nedbryde og fjerne pesticider i laboratorieskala. Men bakterierne begrænses af den trods alt lave koncentration af pesticider og andre næringsstoffer i grundvandet, hvorved bakterierne sultes og gradvis forsvinder fra filteret, der således gradvist men hurtigt mister sin rensningsevne. Membranfiltrering er også en effektiv metode til at fjerne pesticider, men denne teknologi producerer et koncentrat, som en affaldsstrøm der skal viderebehandles. Hvis det membranbehandlede koncentrat bliver brugt som fødestrøm til det biologiske filter, kan det muligvis forbedre bakteriernes chancer for at overleve og opretholde filterets rensningseffekt. Det er denne hypotese, der undersøges i MEM2BIO projektet. Som led i den første arbejdspakke i MEM2BIO afrapporterer denne afhandling studier af forskellige membranprocesser i relation til pesticidfjernelse fra dansk grundvand, og som leverandør af koncentrat til det biologiske filter.

I studiet af NF/RO processer er fire kommercielle membraner blevet undersøgt i forhold til tilbageholdelse af tre pesticider og pesticid omdannelsesprodukter; MCPA, MCPP og BAM. Undersøgelserne viste at NF ikke kan anvendes til fjernelse af specielt omdannelsesproduktetet BAM, mens RO og LPRO membranerne kan tilbageholde alle tre stoffer på et højt niveau. Det blev dog vist, at NF membraner kan have en højere grad af tilbageholdelse, hvis pesticiderne er tilstede i grundvandsrelevante nano- og mikrogramkoncentrationer. Dette gælder specielt de negativt ladende MCPA og MCPP, da de kan blive frastødt af den negativt ladede membran. Derfor har koncentrationen af forureningsstoffet en varierende indflydelse på effektiviteten af membranfiltreringen afhængig af både membranens og stoffets egenskaber, og mekanismen for separationen blev således vist ikke kun at afhænge af molekylets størrelse. Pore flow modeller kunne ikke forudsige tilbageholdelsen, hvis molekylerne var ladede. Ægte grundvand med indhold af mange forskellige ioner og opkoncentrering af grundvandet (højere procentvis genanvendelse) viste samme effekt på pesticidernes tilbageholdelse. Tre typer af dansk grundvand blev undersøgt, og grundvand med højere ionstyrke blev vist at give højere tilbageholdelse pga. blokering af membranens porer med ladede ioner fra vandmatricen, en effekt der også blev eftervist ved højere tilbageholdelse jo mere koncentratet blev opkoncentreret. Dette medførte ligeledes en hurtigere blokering af membranens porer og derved et fald i rentvandsflux. XLE membranen blev valgt til det videre arbejde, da den tilbageholdt alle pesticiderne >92% ved et brugbart rentvandsflux.

XLE membranen blev brugt til produktion af koncentrater til den biologiske nedbrydning ved forskellige grader af opkoncentrering (50%, 80%, 90%). Adsorption af ioner til membranen medførte at koncentrationen af ioner i koncentraterne ikke var så høje som forventet, men de var tilstrækkelige til at undersøge koncentraternes effekt på potentialet for bionedbrydning. Batch og laboratorieskala nedbrydningsforsøg viste en forbedret biologisk nedbrydningskapacitet, når koncentraterne blev brugt som matrice, og den bedste fjernelse og mineralisering af BAM blev observeret i det mest koncentrerede koncentrat (90%). Søjleforsøg viste ligeledes at bionedbrydning på koncentratet kontinuert kunne fjerne BAM over en 40 dages periode.

Brug af aquaporin FO membraner blev undersøgt i forskellige størrelse FO systemer fra et meget lille filtreringsareal til et hollow fiber pilot-skala system. Undersøgelserne viste at tilbageholdelsesresultater bestemt i det lille system kan overføres til pilotskalasystemet. Dette kan fremme brugen af FO i forskellige anvendelser da metoden er simpel, hurtig og billig, og giver brugbare resultater. Den diffusionsbaserede aquaporin FO membran viste tilbageholdelser >98% for alle pesticiderne, samtidig med at den havde et større permeatflux sammenlignet med et par andre FO membraner.

Undersøgelser af uorganiske udfældningsprocesser (scaling) i henholdsvis RO og FO viste at tærsklen for gipsudfældninger var højere for FO processen, når den samme membran blev brugt i en opstilling, hvor det var muligt at måle faldet i flux som et resultat af udfældningerne. Derfor kan det konkluderes, at flux i FO processen er mindre påvirket af scaling end i RO processen. Den anvendte membran var en hjemmesynteseret TFC membran tilsat polydopamin. Membranen viste en høj pesticidtilbageholdelse i både RO og FO mode (>91%) og et permeatflux på ~34 LMH i FO mode.

Den samlede konklusion for denne afhandling er, at kombinationen af RO membranfiltrering med biologisk nedbrydning er en lovende teknologi til rensning af pesticidforurenet grundvand. Undersøgelserne viste, at koncentrater fra membranfiltreringen kan forbedre den biologiske nedbrydning og fuldstændig fjernelse af pesticiderne kan blive opnået i den kombinerede proces. Muligheden for opskalering og undersøgelser af den længerevarende effekt af rensningskonceptet bliver lige nu foretaget i et pilotanlæg koblet til en forurenet drikkevandsboring. Undersøgelserne vil pågå over en periode på 6 måneder, og resultaterne foreligger ikke endnu.

Acknowledgments

A Ph.D. study is officially a one-person endeavor. However, that is just an illusion. This Ph.D. study has not been a lonely journey; it was fruitful as a result of the efforts of some individuals, groups, and organizations, and they all deserve to be credited.

To begin with, I would like to express my utmost gratitude to my principal supervisor, Associate Professor Jens Muff for the opportunity given to me to pursue a Ph.D., he has been supportive and contributed immensely for the successful fruition of this Ph.D. He has been always there not only as an advisor also as a friend making it pleasant for me to get integrated into a new environment. I am highly indebted to my co-supervisor, Assistant Professors Henrik Tækker Madsen, who has always come up with invaluable ideas and comments and has directed in all possible ways to ensure the success of this Ph.D. study.

During the uncountable hours I spent in the laboratory, I enjoyed working next to Dorte Spangsmark, Linda Madsen, and Lisbeth Skou. They were always helpful with all the lab work and are genuinely the treasures of the laboratories. My special thanks also go to all my colleagues at the department especially, Jens Laurids Sørensen for his invaluable help with the HPLC/MS, Sergey Kucheryavskiy for his help in the data presentation with R and Matlab, Marco Maschietti, Morten Strandgaard and lastly Heidi Thomsen, who did magic with all the administrative paperwork.

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I was fortunate to spend four months at the research group of Professor Bart Van der Bruggen at KU Leuven in Belgium. I thank him, and Junyong Zhu from his research group that made me feel welcome and made my stay there a scientific success.

I would also like to express my sincere gratitude to my colleagues from MEM2BIO project namely: Ole Hylling, Morten D. Schostag, Lea Ellegaad-Jensen, Jens Aamand, Lars H. Hansen, Torben Buhl, Peter H. Madsen, Ole Silkjaer, and, Arne Koch.

My heartfelt gratitude goes to my family, specifically my dear mother, Zahra Madah, and my brothers, Alireza, Saeid and Mohammad for supporting my dreams and encouragement throughout my entire life and this Ph.D. journey.

Finally, I thank God for the strength for each day and bright hope for tomorrow.

Preface

> "For the first time in the history of the world, every human being is now subjected to contact with dangerous chemicals from the moment of conception until death." Rachel Carson, American marine biologist, 1907-1964.

In our quest to develop as humans, we undertake different paths that can solve the problems of today, but we do not take into consideration the consequences of today's satisfaction in tomorrow's life. Human activities such as agriculture have resulted in the release of toxic chemicals into the environment. Therefore, we need to deal with pollution in our environment from air to soil and even groundwater.

This thesis is submitted to the Doctoral School of Engineering and Science in partial fulfillment of the requirements for the Ph.D. degree at the Department of Chemistry and Bioscience, Aalborg University, Denmark. The Ph.D. project was performed under the supervisions of Associate Professor Jens Muff from the section of Chemical Engineering at Aalborg University as the principal supervisor and Assistant Professor Henrik Tækker Madsen from the same section as the co-supervisor. The research was carried out in the period spanning from September 2016 to August 2019 at the section of Chemical Engineering at Aalborg University in Esbjerg, Denmark.

The project was designated as part of work package 1 of MEM2BIO project (Innovative combination of MEMbrane technology and BIOlogical filtration for water purification) funded by Innovation Fund Denmark, (contract number 5157-00004B). The project concerns the use of membrane separation in combination with biological filtration for the treatment of groundwater polluted by pesticides in Denmark.

This thesis is structured as a collection of scientific papers. Chapter one of the thesis is the introduction section, talking about the magnitude of the pesticides pollution problem in Denmark, different solutions for pesticides removal, the problem statement, and the objectives of the study. Chapter two reviews the relevant literature on the study. Chapter three to six represent the condensed papers. Each chapter is concerned with a specific topic related to a paper presented at the end of the thesis. Chapter three describes the use of NF and RO membrane for pesticides removal and studies the effect of different real-life parameters on the performance of membrane filtration. Chapter four presents the result of the combined membrane and biofiltration system which was the main objective of this study. Chapter five covers a summary of the use of aquaporin FO membrane in various systems of different scales and investigates the impact of the use of real water matrix and different draw solutes. Chapter six presents the results of the synthesized membrane to be used for the removal of pesticides and compared in terms of scaling propensity in RO and FO processes. Chapter seven describes the pilot plant of MEM2BIO project. In the end, the whole thesis is concluded with the conclusion and my perspectives on future research topics within this field.

I end with another quote from Nathaniel H. Egleston (1822-1922)

> “Nature bears long with those who wrong her. She is patient under abuse. But when abuse has gone wrong too far, when the time of reckoning comes, she is equally slow to be appeased and turn away her wrath.”

I hope you enjoy reading this thesis.

Mahdi Nikbakht Fini,
August 2019

Thesis details

Thesis title: Studies on membrane separation for a combined membrane and biofiltration of pesticides in groundwater based drinking water treatment

Ph.D. student: Mahdi Nikbakht Fini

Supervisor: Jens Muff

The main body of this thesis is based on the following papers:

Paper I: M. Nikbakht Fini, H.T. Madsen, J. Muff, “The effect of water matrix, feed concentration and recovery on the rejection of pesticides using NF/RO membranes in water treatment”, Sep. Purif. Technol. 215 (2019) 521–527.

Paper II: O. Hylling, M. Nikbakht Fini, L. Ellegaard-Jensen, J. Muff, H.T. Madsen, J. Aamand, L.H. Hansen, “A novel hybrid concept for implementation in drinking water treatment targets micropollutant removal by combining membrane filtration with biodegradation”, Sci. Total Environ. 694 (2019) 133710.

Paper III: M. Nikbakht Fini, H.T. Madsen, J. L. Sørensen, J. Muff, “Moving from lab to pilot scale in forward osmosis for pesticides rejection using aquaporin membranes”, *Under review* in Journal of Membrane Science.

Paper IV: M. Nikbakht Fini, J. Zhu, H.T. Madsen, Bart Van der Bruggen, Jens Muff, “Preparation, characterization and scaling analysis of a polydopamine incorporated RO/FO TFC membrane for pesticides removal”, *draft manuscript*

In addition to paper II the following paper is also under preparation:

Paper V: L. Ellegaard-Jensen, M. D. Schostag, M. Nikbakht Fini, N. Badawi, J. Aamand, L. H. Hansen, “Prolonged persistence of *Aminobacter* sp. MSH1 in bioaugmented sand filter columns provides stable removal of pesticide residue”, *Under preparation*

In addition to the journal articles, following selected oral presentations and poster presentation have also been made in the conferences.

Paper VI: M. Nikbakht Fini, H.T. Madsen, J. Muff, “Removal of frequently found pesticides from Danish drinking water using NF/RO membranes”, *oral presentation*, 12th annual meeting of Danish Water Forum, 30 January 2018

Paper VII: M. Nikbakht Fini, H.T. Madsen, J. Muff, “Performance Evaluation of NF/RO Membranes for Separation of BAM, MCPA and MCPP From Danish Drinking Water”, *Proceedings of MTC18.* American Membrane Technology Association, 14 Mar 2018

Paper VIII: M. Nikbakht Fini, H.T. Madsen, J. Muff, “Removal of pesticides from aqueous solution using aquaporin FO membrane” *Poster presentation,* Euromembrane 2018 Conference, July 2018

Paper IX: M. Nikbakht Fini, H.T. Madsen, J. Muff, L. Ellgaard-Jensen, O. Hylling, L. H. Hansen, “Performance of NF/RO membranes in a combined membrane separation and biological degradation process for treatment of pesticide contaminated drinking water” *Oral presentation*, Nordic Filtration Symposium, Aug 2018.

In addition to the papers related to the subject of this Ph.D. thesis, the following publications have also been made:

Paper X: M. Nikbakht Fini, S. Soroush, M.M. Montazer-Rahmati, “Synthesis and optimization of chitosan ceramic-supported membranes in pervaporation ethanol dehydration”, Membranes, 8 (2018) 119.

Paper XI: N.L. Pederson, M. Nikbakht Fini, Monlar P.K., Muff J. “Synergy of combined adsorption and electrochemical degradation of aqueous organics by granular activated carbon particulate electrodes”, Separation and Purification Technology, 208 (2019) 51-58.

Paper XII: A. Asamoah, M. Nikbakht Fini, D.K. Essumang, J. Muff, E.G. Søgaard, “PAHs contamination levels in the breast milk of Ghanaian women from an e-waste recycling site and a residential area”, Science of the Total Environment, 666 (2019) 347-354.

Table of contents

Chapter 1. **Introduction**

Pesticides probably are the largest amount of chemicals deliberately discharged to the environment. An immense quantity of pesticides is applied to agricultural fields all over the world, including Denmark, to stimulate crops and fruits production. Pesticides mean a lot to Danish agriculture. They help control weeds, fungal diseases, and insect pests so that Danish fruit, vegetables, and cereal products are on shelves every day. Pesticides hinder pests growth by inducing physiological responses in pests. Those reactions might be harmful not only to target also nontarget organisms such as livestock and humans [1]. Pesticides undergo biodegradation by the native microbial community after being applied and are rarely broken down into the water, carbon dioxide and other inorganic species. In most cases, however, pesticides are just metabolized to other organic substances called pesticide transformation products (PTPs). These recalcitrant pesticide residues, therefore, persist in the environment and contaminate soil and water resources.

Danish society is carefully conscious of their environment. A recent poll conducted by Norstat for Altinget and Jyllands-Posten in late 2018, a few months before the Danish parliamentary election, shows that the environment and climate are at the top of the electorate’s concerns and is the most important claim of the Danish voters [2]. Amongst the environmental concerns, another poll in October 2018 reveals that drinking water contamination is the second top issue that concerns the Danes by 18% after the climate change [3]. Therefore, a sustainable drinking water production aligned with quality requirements must be prioritized in the Danish public and political paradigm.

The appearance of pesticide residues in drinking water resources such as groundwater has received significant attention as it imposes an adverse threat to public health. Pesticide residues can risk neuroendocrine development in unborn and newborn children and can end up to chronic kidney disorders and other unforeseen impacts in later life, as well [4,5].

Danish pesticides handling policy has been based on preventive measures like the prohibition of the use of pesticides in the lands where a water well protection vicinity zone is defined [6]. However, pesticides and PTPs have persistently appeared in groundwater in Denmark. In Denmark, like many other countries, a set of selected pesticides and PTPs is subject to a careful monitoring program to secure the production of clean drinking water. Nevertheless, the appearance of 75 new pesticides in the groundwater which have not been detected before, (e.g., DPC and DMS) was the headline of the news in Danish media in April 2019 [7]. This reveals that the Danish pollution legislation may not have been as ambitious as thought, and this could have consequences for the quality of drinking water. Therefore, apart from the preventive, remedial measures must also be taken; thereby, this Ph.D. thesis studies a promising concept to be implemented for remediation of groundwater polluted by pesticides.

In this section, the current status of pesticides pollution in Danish groundwater, including amount, spread, and type of pesticides will be described. Afterwards, the consequences of pesticides pollution, and subsequently, the current drinking water treatment processes used in Denmark will be discussed. Then, the proposed concept for remediation of water polluted with pesticides will be introduced. The objectives of this thesis will be lastly presented.

1.1. Pesticides pollution in Denmark

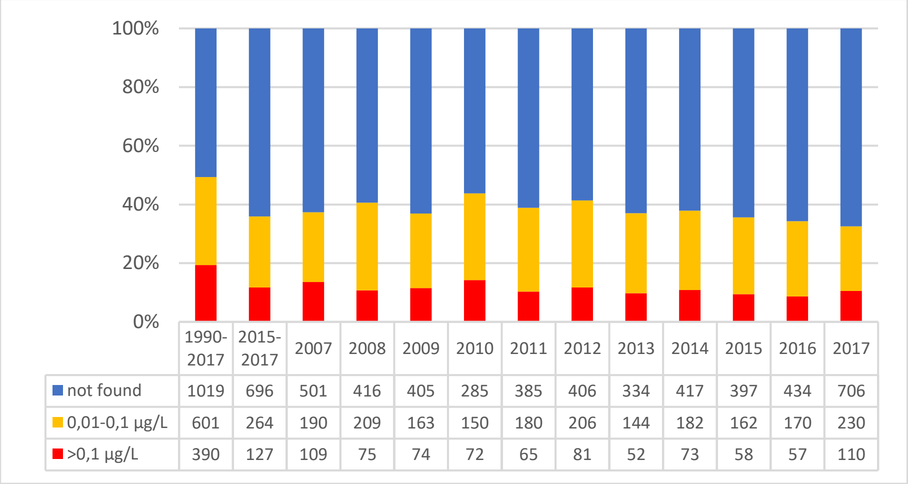
In groundwater, pesticides and pesticide transformation products (PTPs) can stem from the commercial use of pesticides in forestry and agriculture, from the use of companies and private consumers in gardens and factories, as well as from use on fortified districts and at infrastructure facilities. Some pesticides are also used, or have been used, as seed dressing agents and as biocides (e.g., in paints and wood preservatives) [8]. The term pesticide transformation products (PTPs) relates to substances that are degraded through biological or nonbiological processes during the percolation of their parent pesticides from the surface, where they have been applied to the groundwater aquifers [9]. For most pesticides, transformation results in detoxification to non-toxic products. Major degradation products of some previously used pesticides, however, play a crucial role in groundwater contamination [9]. A well-known example of such transformation products in Denmark is 2,6-dichlorbenzamid (BAM), a degradation product of prohibited herbicide dichlobenil, that was mainly used in courtyards, driveways, and other fortified areas, as well as in fruit and berry production in the period 1969-1996 [8]. Although the application of dichlobenil has been banned since 1997, the metabolite BAM has been one of the main contributors of groundwater contamination in Denmark [10,11].

In Denmark, the groundwater monitoring is annually performed by GEUS (The Geological Survey of Denmark and Greenland) to investigate the groundwater pollution caused by different substances, including pesticides and their degradation products [10]. This scheme is called the national groundwater monitoring program (GRUMO) covering 1046 intake samples in the latest report in 2017 [8]. The waterworks also carry out the same survey for drinking water abstraction wells that included 2871 drinking water wells in 2017 to ensure the quality of water delivered to the consumers throughout Denmark [8]. The monitoring has now been in place for nearly 30 years from 1989 and included a systematic sampling, data collection, and reporting that provides a comprehensive picture of groundwater quality in Denmark. The latest annual report, including both GRUMO scheme and waterworks drinking water wells, presented the development of pesticides pollution in groundwater samples from 1989 to 2017.

Over the years, a varying number of substances have been included in the analysis program. By the development of analytical methods, new pesticides and transformation products are included when the program periods are revised. At the same time, substances that are only rarely or never detected in the groundwater have been excluded from the analysis plan. In the latest survey in 2017, a total of 34 pesticides (13) and degradation products (21) were included by GRUMO program while this number was 36 for the survey carried out by the waterworks, by having Desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) added to the waterworks survey as newly found PTPs [8]. As a comparison, just two years earlier, in 2015, the number of pesticides and PTPs underwent the GRUMO and drinking water wells programs was 31 in total [12]. Furthermore, the monitored pesticides are categorized into three types in terms of their application permit: approved, regulated, and prohibited. Interestingly, in 2017, both monitoring programs include only two currently-approved, seven regulated (mainly phenoxy acids) and twenty-seven prohibited pesticides/PTPs indicating that around 95% of the pollutant pesticides are those that are either prohibited (80%) or limitedly applied (15%). This implies the persistence of the compounds of concerns that are still found in the groundwater intakes and shows the significance of pesticides problem in Denmark.

According to the Drinking Water Directive [13] and the Groundwater Directive [14], the permitted value for the pesticide content in drinking water and groundwater set by the EU Council is 0.1 µg/L for individual pesticides and PTPs, while for the total sum of individual pesticides and PTPs it is 0.5 µg/L. In Denmark, the threshold value of 0.1 µg/L applies for both pesticides and biocides [8].

According to GRUMO monitoring results in 2017, pesticides or their degradation products were found at least once in 32.5% of the 1046 sampled intakes, and the permitted value of 0.1 µg/L was exceeded at least once in 10.5% of the sampled intakes of GRUMO program [8].



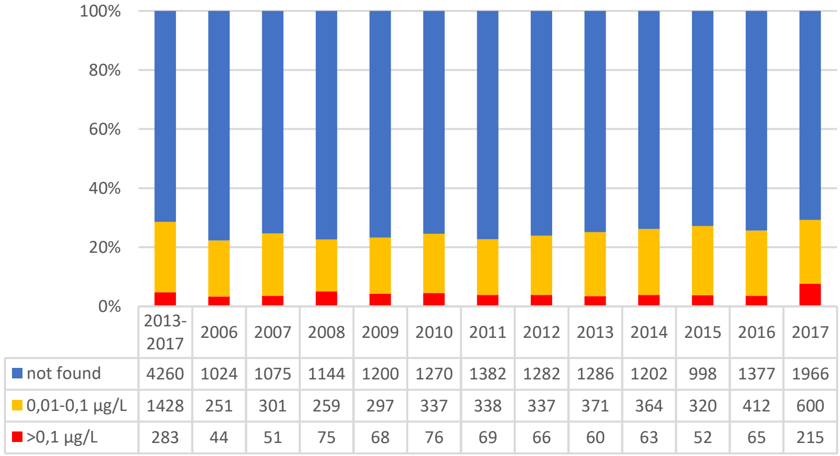
	1990-2017	2015-2017	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
🟦 not found	1019	696	501	416	405	285	385	406	334	417	397	434	706
🟨 0,01-0,1 µg/L	601	264	190	209	163	150	180	206	144	182	162	170	230
🟥 >0,1 µg/L	390	127	109	75	74	72	65	81	52	73	58	57	110

Figure 1-1 The GRUMO monitoring program data for individual years from 2007-2017 as well as cumulative results for 1990-2017 and 2015-2017. The data is extracted from [8].

Figure 1-1 depicts the development of pesticides pollution in the sampled intakes from 2007 to 2017. Cumulative results for 1990-2017 and 2015-2017 are also shown for comparison with the individual years. Throughout the monitoring period 1990-2017, pesticides or degradation products have been detected at least once in 49.3% of the 2010 surveyed intakes, of which at 19.4% at least one exceeded the required value [8].

From the presented data in Figure 1-1, it can also be concluded that pesticide pollution has been stabilized during the period 2007 to 2017. The fluctuations happen mostly because new compounds have been added to the monitoring program or wells taken out of order. The concentration of pesticides in the groundwater does not seem to decline remarkedly, and data for specific pesticides indicates only a slight decrease over the years [9]. This is even though the use of many of the pesticides was prohibited over the past three decades, and the groundwater contamination by pesticides may thus be expected to be observed for many years ahead.

In addition, the analysis of presence of approved and prohibited pesticides/PTPs in GRUMO data in 2017 shows that at least one permitted pesticide or degradation product was found at least once in 5.9% of the studied intakes, while the requirement value of 0.1 µg/L was exceeded at least once in 1.6% of the intakes. Prohibited pesticides/PTPs, on the other hand, were found at least once in 27.3% of the intakes with an exceedance of the threshold limit in 7.2% of intakes [8]. Prohibited substances were thus, found to be far more frequently found than the allowed pesticides, which might be partly due to the fact that prohibited substances constitute by far the largest proportion of substances in the analysis program. In addition, prohibited substances appear in the groundwater for many years after their application has been prohibited.



	2013-2017	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
🟦 not found	4260	1024	1075	1144	1200	1270	1382	1282	1286	1202	998	1377	1966
🟨 0,01-0,1 µg/L	1428	251	301	259	297	337	338	337	371	364	320	412	600
🟥 >0,1 µg/L	283	44	51	75	68	76	69	66	60	63	52	65	215

Figure 1-2 The drinking water wells monitoring data for individual years from 2006-2017 as well as cumulative results for 2013-2017. The data is extracted from [8].

The most recent developments in the monitored pesticides/PTPS in groundwater from waterworks wells is also presented in Figure 1-2. In 2017, at least one pesticide was found in 29.3% of the investigated waterworks wells, where 7.4% of the wells surveyed exceeded the required value. During the last five years of the monitoring report, 2013-2017, pesticides were found at least once in 23.9% of the sampled wells, where 4.7% of the wells recorded at least one exceedance of the required value. Surprisingly, the share of polluted water wells, and in particular those exceeding the requirement value, was higher in 2017 compared to the previous years. This is due to the inclusion of DPC in the monitoring of drinking water wells in 2017, which was often measured above the limit value. It should be noted that only a small part of the waterworks wells in 2017 was investigated for DPC and MDPC and the polluted portion should, therefore, be expected to increase further in the years ahead. Currently, there is extensive work going on related to screening of Danish groundwater for ”new” pesticides and deciding which should be added to the monitoring programs by the regions and GEUS.

In the case of monitored waterworks wells, at least one of the prohibited pesticides occurred at least once in 21.8% of the waterworks wells investigated, and in 4.3% of the waterworks wells, there was at least once exceeded the requirement value of 0.1 µg/L [8]. This number was 4.0% for the approved pesticides in the sampled drinking water wells, while the requirement value was exceeded at least once in 0.5% of the wells. This trend is in line with what was found for GRUMO intakes, where the banned pesticides in the nineties constituted the main share of the water contamination.

In comparison to Figure 1-1, the depicted data in Figure 1-2 shows that the percentage of polluted drinking water wells is lower than the groundwater in GRUMO. This is due to the closure of polluted wells by the waterworks when the pollution exceeds the allowed value, and the quality requirement of drinking water cannot be met through the mixing of wells. It is also worthwhile to mention that although the percentage of drinking water wells exceeding the threshold limit is relatively low, the total number of affected drinking water wells in 2017 (215) is significant. Thus, a considerable portion of the population in Denmark might be in the risk of exposure to a background concentration of pesticides if appropriate preventive, as well as remedial measures, are not taken in Danish drinking water sector.

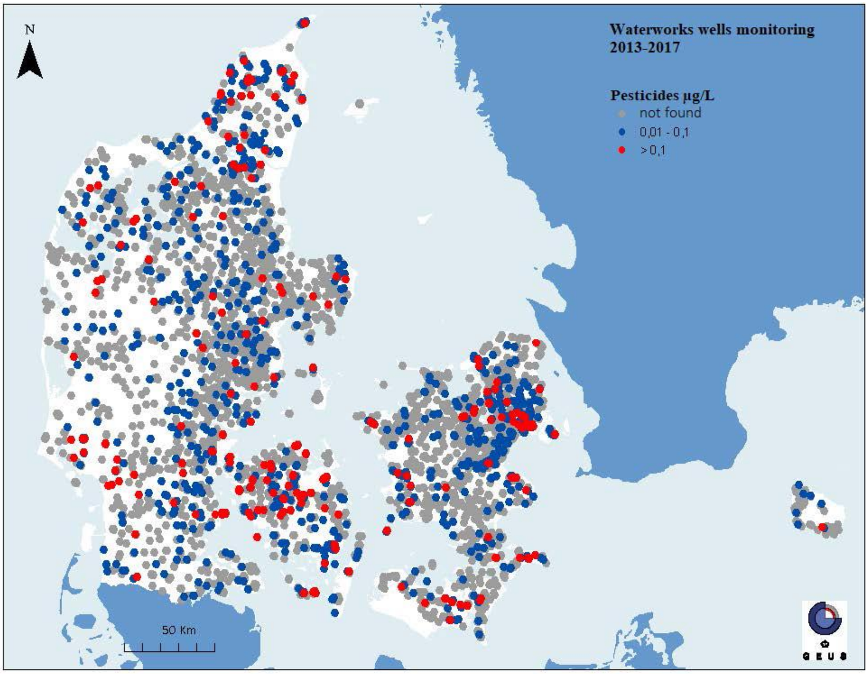


Figure 1-3 Pesticide pollution distribution map in Denmark within 2013-2017 [8].

Figure 1-3 shows the geographical distribution of pesticide pollution in active waterworks wells in the period 2013-2017. It is clear that the frequency of exceedances of the threshold value is over-represented in northernmost Jutland, in a belt across south Jutland, Fun, as well as the north-eastern part of the metropolitan area. Traditionally, pesticide pollution is expected to be associated with agriculture and farm activities, thus mostly observed in rural regions. However, an opposite pattern is observed in the distribution map, where the pollution is focused around the main cities in Denmark. This is partially due to a great number of drinking water wells in the vicinity of the cities than the rural areas, but it is also influenced by the fact that earlier practices by both property owners, industry and municipalities have had a significant effect on the groundwater contamination. Furthermore, major Danish cities are situated close to the coastline in the entire country, where the aquifers are unconfined and placed not so deep from the surface. These aquifers are, therefore, more vulnerable to pesticides leaching down from the surface [15].

The top 5 most frequently found pesticides/PTPs in the last two years of reported monitoring plan for waterworks wells are tabulated in Table 1-1. Up to 2016, 2,6-dichlorbenzamid (BAM), a degradation product of dichlobenil, has been the traditional most often detected pesticide in Danish groundwater and drinking water wells. In the past 25 years (1992-2017), it was found in 19.4% of waterworks wells, and it has exceeded the permitted value in 3.4% of the samples. However, in 2017, its top place in the list was replaced by a newly analyzed PTP, Desphenylchloridazon (DPC). DPC is a degradation product of a banned herbicide chloridazon that used to be sold in Denmark from 1964 to 1996. DPC was first analyzed by waterworks for only 12 wells in 2016 and since it recorded a high amount of detection, together with MDPC were placed in the list of obligatory analyzed compounds by the waterworks from October 2017 [8]. DPC was found in 25% of wells in 2017 with exceedance rate of 9.5%.

Table 1-1 The top five most frequently found pesticides in drinking water wells in 2016 and 2017 [8,16]

Drinking water wells 2016			**Drinking water wells 2017**		
Pesticide	Found (%)	Found >0.1 µg/L (%)	Pesticide	Found (%)	Found >0.1 µg/L (%)
2,6-Dichlorbenzamid (BAM)	16.2	1.8	DPC	25.0	9.5
Desphenylchloridazon (DPC)*	8.3	0.0	BAM	16.9	1.7
Bentazon	2.3	0.4	MDPC	5.7	0.6
CGA 108906	1.7	0.1	Bentazon	2.7	0.2
Mecoprop (MCPP)	1.6	0.0	Mecoprop (MCPP)	1.7	0.1

*In 2016, only 12 drinking water wells were analyzed for desphenylchloridazon (DPC).

BAM was also still a major contributor in 2017, and its appearance in drinking water wells has remained unchanged over the past years. Phenoxy acids have also been amongst monitoring program from which mecoprop (2-(4-Chloro-2-methyl phenoxy) propanoic acid or MCPP) has been detected amongst top pollutants.

1.2. Consequences of pesticides pollution

The Danish drinking water doctrine proclaims that drinking water supply must be “naturally pure groundwater”, and it is prioritized to relocate abstraction wells rather than undertaking advanced treatment. Therefore, waterworks are obliged to close highly pesticides contaminated drinking water wells and look for unpolluted groundwater resources somewhere else in the vicinity. This means that a direct consequence of pesticides pollution is to impose waterworks (consumers through bills) additional costs to find clean water resources, acquire the land above the new well, drill and establish a new well and delivery of water from probably longer distances to the waterworks. However, in the long term, it can associate with a worse consequence, which is having the drinking water supply under pressure in particular in those regions that clean aquifers cannot readily be found.

It is estimated that every year, 30 drinking water wells must be closed solely due to pesticides pollution [17]. In an annual report by the Danish Environment Protection Agency (EPA), it is reported that in total, 116 water wells were closed in 2017, of which 26 caused directly by pesticides pollution [18]. When a well has to close, it costs up to 5 million Danish Krone (670,000 Euro) to establish a new well that is indirectly paid by consumers, according to Danish Water and Wastewater Association (DANVA) [17]. In the areas where a new clean well can be easily found and drilled or the portion of existing uncontaminated wells in the water supply can be increased, the closure of one well might not be a serious issue. However, when the whole vicinity is polluted, and cleaned resources cannot be located, the consequences can be immense. For instance, the groundwater in the vicinity of the capital region, Copenhagen, is widely under pressure with pesticides pollution (See Figure 1-3), it has not been possible in all cases to follow the same strategy of relocating abstraction wells. As a result, activated carbon filters following with a UV treatment have been implemented as an advanced treatment at two waterworks, Hvidovre and Frederiksberg, for pesticides and chlorinated solvents contamination, respectively [19]. Membrane technology is also being tested in the capital region by HOFOR to remove pesticide residue N, N-Dimethylsulfamide (DMS). It is reported that in the whole country, 10 Danish waterworks have already adopted an advanced water treatment for the removal of pesticides because they have not been able to find clean groundwater nearby [20].

1.3. Drinking water production in Denmark

Denmark has a highly decentralized drinking water supply with waterworks located all over the country. Quite uniquely, the country employs groundwater as its sole resource of drinking water with Christiansø (Christians island) as the only exception, where desalinated seawater is also used as drinking water [8]. The high quality of deeper groundwater aquifers obviates the need for complicated and costly water purification thus, a so-called “simple treatment” is implemented in waterworks and tap water is not chlorinated owing to a highly efficient distribution network where microbes and other pollutants are minimized.

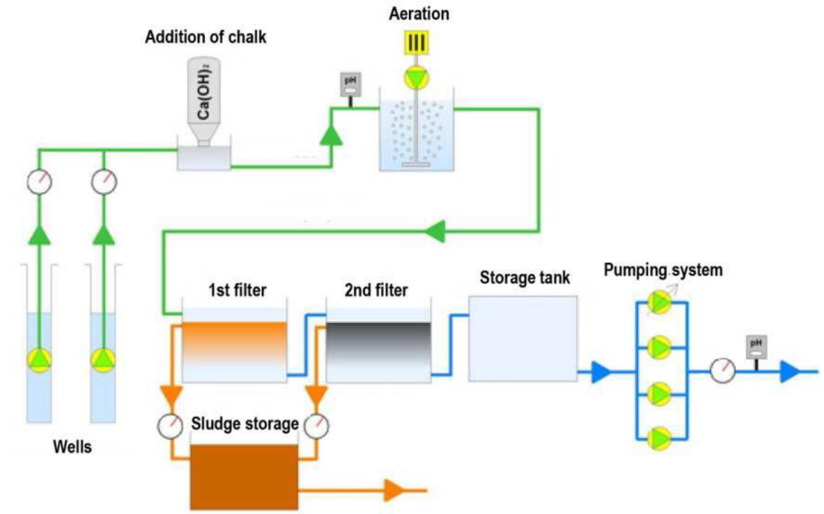


Figure 1-3 General process diagram for a Danish waterwork (Din Forsyningen Esbjerg). The addition of chalk is not part of a standard simple treatment plant [19].

The Danish simple water treatment is consisting of aeration followed by two stages of sand filtration. An overview of the process and the changing water composition is schematically illustrated in Figure 1-4. The water is transferred from groundwater wells to the waterwork through pumping. Here, the water is undergone aeration step where gasses like methane and hydrogen sulfide are vented out from the water stream. In the aeration step, the water is also saturated with oxygen to oxidize iron, manganese, and ammonium ions partially. The main oxidation, however, takes place in the sand filters where ammonium is oxidized to nitrate by microorganisms, and iron and manganese are oxidized through the autocatalytic environment and the formed ferrihydrite coats the sand grains. Here, at the end of two sand filtration stages where the iron, manganese, and ammonium are removed, the simple treatment is completed, and the clean water is stored before being delivered to the consumers [19].

The simple treatment process has been solely designed to fulfill the Danish drinking water policy in which water supply must be based on naturally pure groundwater with no advanced treatment which is quite common in most countries where the drinking water is primarily supplied from surface water and/or shallow aquifers. As a result, the simple treatment method in Danish waterworks is not capable of removal of pesticides. For instance, in two studies in Denmark, it was found that the concentration of pesticides in the groundwater were not affected by aeration and sand filtration [21,22].

To sum up, the establishment of new wells is a costly process. Moreover, clean groundwater wells are not accessible as before since so many sites are being found to be contaminated by pesticide residues; thus, clean groundwater supply in Denmark is under pressure as is overexploited. On the other hand, the existing simple treatment approach is not effective towards pesticides. Therefore, it is undeniable that sooner or later, new treatment concepts are required to be integrated into Danish drinking water production to remove pesticide residues and sustain delivery of high-quality water to the consumers.

1.4. Methods for pesticides removal

As previously mentioned the conventional simple treatment method in Denmark, comprising aeration and sand filtration, is not effectively capable of removing pesticide residues from the water. In some cases, when unpolluted water wells have not been in access, Danish waterworks had to apply advanced water treatment to purify water contaminated by pesticides. In this case, waterworks need to acquire specific permission where the technical, economic, environmental, and health aspects of the applied method must be assessed. The latter is evaluated in a statement from the National Board of Health, represented by the medical health inspectors [12]. The condition for a treatment method to be permitted by Danish drinking water authorities is that the pesticides removal technique should be performed with preferably no change in the water composition. Therefore, it would be more likely for an advanced treatment method to be accepted if it does not include the addition of chemicals to the water.

To date, the adsorption with granular activated carbon (GAC) has been mostly considered to be effective for pesticide removal as an additional advanced filtration step by Danish waterworks. Apart from GAC, some have also studied the possibility of the use of different types of adsorbents such as a mesoporous metal oxide (Al_2O_3) [23], nanostructured materials in particular carbon nanotubes [24], and polymeric adsorbents [25]. However, the adsorption method has some significant shortcomings and problems that include limited availability, low capacity, and saturation of adsorbent, high costs of regeneration or renewal of adsorbent and to some extent toxic chemical by-products which may develop in the filters [24–26]. Moreover, activated carbon is not effective towards all the pesticides. The GAC is most effective for non-polar compounds and as the PTPs tend to be more polar and water-soluble, they can be removed to less extent compared to their parent compounds [11]. The development of other treatment methods has been, therefore, highly prioritized over the last few decades. For this purpose, a variety of different biological, chemical, and physical methods have extensively been studied by scientists for the removal or degradation of pesticides and pesticide transformation products from water.

An alternative for adsorption with GAC is the advanced oxidation processes (AOPs) that have also attracted special attention of researchers in Denmark, especially at

Aalborg University. The AOPs constitute a set of methods for generating highly reactive hydroxyl radicals that have been shown to be applicable for the degradation of a broad range of organic contaminants [27–30]. The AOPs are divided into two primary categories of processes: with and without the addition of chemicals [15]. The oxidation processes including H_2O_2 [29], O_3 [31,32] and Fenton [30,33] are performed through the addition of chemicals while in photocatalysis [34,35] and electrochemical oxidation [36–39] no chemical agent is added to the process. Although applicable for pesticides degradation, AOPs are energy-intensive systems hindering its application in large scale water treatment plants [40]. Besides, AOPs suffer from the formation of by-products [15,28,37]. Theoretically, the high oxidation potential of the hydroxyl radical results in complete mineralization of the contaminants; however, as the degradation is not a one-step process; oxidation intermediates will be formed during the reaction. These degradation intermediates can be more toxic compared to the parent pollutants; thus, it requires to be handled [15]. In order to optimize the energy consumption of AOPs, researchers have suggested different pre-concentration strategies to have concentrated polluted water with a reduced volume to be treated by AOPs. In this way, the micropollutants are removed from the main water matrix through a pre-treatment unit, and the concentrated residue will be sent to AOP for further treatment. The pre-concentration can be carried out for instance, by membrane filtration [33,40,41]. As the rate of the oxidation reaction is positively correlated with micropollutants concentration, a higher reaction rate when the polluted water is concentrated would result in shorter reaction time hence lower energy consumption per unit mass of removed pollutant. Another advantage of combining AOPs with membranes is that the pesticides are removed from the main water stream before degradation takes place. This ensures that possible intermediates do not end up in the main body of the water, that can be more easily controlled.

The membrane technology has been introduced as an effective approach for remediation of water polluted with pesticides. Since the majority of identified pesticides have molecular weights greater than 200Da, the main research in this field has been carried out on the pressure-driven membrane processes, i.e., nanofiltration (NF) and reverse osmosis (RO) as high-potential candidates [26]. NF and RO have been proven as promising treatment approaches for pesticide removal in an effective and reliable way. However, one of the main challenges that arises from RO is high energy consumption in order to provide the required pressure. One of the efforts which, to a large extent, improved these membranes led to the development of ultra-low pressure RO membranes (ULRO) [26]. ULRO membranes need relatively lower operating pressure compared to typical RO membranes that result in lower operating costs, which are a considerable step to make membrane technology a competitive and cost-effective way for pesticide removal. The newly-developed membrane process, forward osmosis (FO), has also been proposed that can have a lower cost of energy compared to RO membrane filtration. Driven by an osmotic pressure gradient, in FO water molecules are permeated through a semipermeable membrane from the polluted water (feed solution) to a highly concentrated salt solution (draw solution) [42].

Therefore, it does not require hydraulic pressure, thereby, potentially needs a lower cost of energy.

Another shortcoming associated with membrane filtration is that membranes tend to foul over time. The fouling/scaling problem has relatively been tackled with a range of measures such as using chemicals for membrane cleaning, using antiscalants, accelerated seeded precipitation, and pH adjustment [31,43,44]. In some cases, a pre-treatment step might be beneficial to avoid or postpone fouling of the membranes. The FO process has also been thought to be less prone to fouling phenomenon as no hydraulic pressure is pressurizing species on the surface of the membranes. Moreover, a large volume of highly concentrated retentate stream is a result of membrane filtration, which is one of the concerns associated with membrane technology. This waste stream might take up to 35% of the feed stream and is several times more concentrated rather than the influent [31]. An effective strategy to handle the residual retentate stream can be achieved through the combination of membrane filtration with a subsequent degradation method like AOPs or biodegradation. Perez-Gonzalez et al. have reviewed various methods on the treatment of the retentate from the RO membrane process such as APOs, FO, adsorption, crystallization, electrodialysis, membrane distillation, and extraction [45]. In this way, for instance, the combination of membrane and AOPs benefits AOPs as previously discussed and handles the concentrated retentate from membrane filtration, as well [46].

The incorporation of specific bacteria capable of degradation of pesticides into the sand filters in waterworks has also been suggested as a biological treatment method for pesticide-contaminated water treatment [11,47–49]. For instance, Albers et al. have introduced a BAM-degrading bacterium, *Aminobacter* sp. MSH1, to a pilot-scale sand filtration plant [11]. They showed that bioaugmentation of MSH1 into the sand filters led to 75% removal of BAM with an initial concentration of 0.2 µg/L resulting in purified water with concentration below the permitted value of 0.1 µg/L [11]. However, their method suffered from the disappearance of microbial cell densities and consequently BAM removal capacity within 2-3 weeks of initial inoculation. They explained that different reasons might contribute for this issue like loss of BAM degrading bacterium as a result of the backwash of sand filters, competition with the natural microorganisms already existing in the filters, protozoan predation and starvation due to the low BAM concentrations [11]. Another research group also pointed out the starvation of the microorganisms to be the main contributor in the loss of BAM removal capacity after 2-4 weeks, when the concentration of BAM in feed water was only 0.2 µg/L [49]. Simply put, the pesticides degraders needed more nutrients and a higher concentration of pesticide to survive and keep on degrading pesticides in the long-term. Therefore, the pre-concentration technique might be beneficial in this case, as well. The pre-concentration can be performed by using membrane filtration. In this way, the main part of the polluted feed water will be treated by membrane filtration and the residual stream containing concentrated pesticides and the other nutrients present in the water matrix will be sent to biodegradation unit. This combination is the subject of the MEM2BIO research project that will be presented accordingly in the next section.

1.5. MEM2BIO project

As previously mentioned, pesticides residues in Danish groundwater has increasingly been found over the past decades. Danish authorities, however, have established the drinking water based on natural groundwater through simple treatment and advanced treatment methods are not allowed to be undertaken. In some cases though, the waterworks have not been able to relocate drinking water wells because clean water aquifers have not remained in the vicinity of the target town. Alternatively, they have used adsorption by activated carbon for pesticides removal followed by UV treatment for disinfection. Activated carbon is not effective for some pesticides such as phenoxy acids and DMS. Therefore, a new treatment approach needs to be proposed to be implemented in Danish drinking water production system to ensure reliable and sustainable water supply.

An attempt to establish a concept to be integrated into waterworks was to inoculate pesticide degrading bacteria to the sand filters for biodegradation of BAM. Although being capable of breaking down BAM to below the threshold limit, the biodegradation capacity did not last for more than three weeks. This observation was explained by the loss of the degrader's density due to backwash, competition with the native microbial community and most importantly, starvation because of low concentration, of pesticides and other nutrients in the water [11,48,49]. Seeking a solution to resolve starvation of the degraders led to the genesis of MEM2BIO project where membrane filtration rejects pesticides from the main body of the water and also provides concentrated feed water for biological sand filtration.

The MEM2BIO is a novel concept aiming at pesticides removal which combines MEMbrane filtration with BIOdegradation in sand filters. The idea is to send pesticides polluted water to a membrane filtration unit in the first place (Figure 1-4). This will produce two streams. The primary stream is the purified permeate water where the concentration of target pesticides as well as all the other present species such as ions is at the lowest level. The level of pesticides removal depends on both target pesticides and the membrane employed in the membrane filtration, thus requires a careful membrane selection. On the other hand, a concentrated retentate is another resultant stream of membrane filtration step. In the retentate, all the compounds present in the water matrix, including pesticides, other carbon-based compounds, and ions, will be concentrated. This is actually what may be the best feed for the biodegradation process. Therefore, the retentate from membrane filtration will be used as a feed influent to the sand filters inoculated with pesticides degrading bacterias acting as a booster for sustainable biological sand filtration. The microorganisms in the sand filters will only target the pesticides. Hence, the other inorganic ions will remain unaffected, allowing us to mix the effluent water from bio-sand filters with the permeate water from membrane filtration and re-mineralize the permeate water. The merged purified streams constitute the final clean water stored in a tank before being distributed to the consumers.

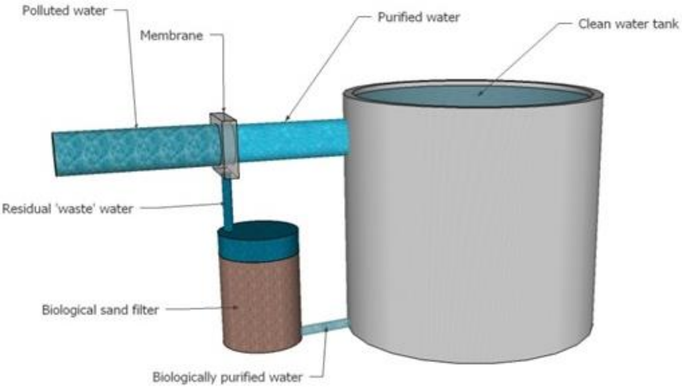


Figure 1-4 Schematic illustration of MEM2BIO project [50]

Hypothetically, this ides takes advantage of both already established processes to overcome the drawbacks associated with any of them. On the one hand, biodegradation serves as a handling technique for highly concentrated retentate of the membrane process and simultaneously, membrane filtration retentate serves as a booster for biodegradation by the nourishment of degrading organisms. In addition, the flow of water to be biodegraded will be lower that can prolong the residence time of polluted water in the bio-sand filters resulting in an increased biodegradation efficiency. Furthermore, there are no chemicals added in this method, meaning that it does not interfere with Danish doctrine for water treatment.

The MEM2BIO is an industrial research project funded by Innovation Fund Denmark (project ID: 5157-00004B) running from 2016-2020. The MEM2BIO aims at the acquisition of new knowledge for developing water remediation technologies superior to other technologies such as granular activated carbon (GAC) treatment. The research will result in a technical prototype water treatment plant established in the field where polluted drinking water well is available. Steps beyond MEMBIO will be the development of commercial prototypes including more in-depth surveys of regulatory and legislative issues related to the use of membranes and microbial processes in water supply internationally and eventually commercialization where the technologies are launched on the market.

The MEM2BIO consists of four different collaborative work packages (WPs) and gathers two universities, one research institute, two Danish water suppliers managing waterworks, a water treatment company (Silhorko-Eurowater), and a membrane developer company (Applied Biomimetic A/S). The WP1 concerns membrane filtration that is subject of this thesis report, WP2 contains biodegradation in sand filters, WP3 is concerning upscaling the whole process to a pilot-scale water treatment plant, and WP4 is the management and coordination of the entire project. Aalborg University (AAU) is responsible for WP1, Aarhus University (AU) is in charge of WP2, GEUS is taking care of WP3 and WP4. The inclusion of two waterworks, TREFOR and Din Forsyning, as potential end-users, contributes the rapid marketing of the developed technology. Both Silhorko and Applied Biomimetic A/S (AB) operate at the water supply market, and their inclusion in the MEM2BIO project will facilitate the implementation of the developed technologies at waterworks nationally and internationally.

The MEM2BIO targets the removal of BAM as it has been found most frequently in the past 25 years in drinking water wells. Moreover, in WP1, two phenoxy acid herbicides 2-methyl-4-chlorophenoxyaceticacid (MCPA), and 2-(4-Chloro-2-methylphenoxy)propionic acid (MCPP) that are also of concerns in Danish groundwater wells are subject to membrane filtration studies.

It should be mentioned that based on discussions during the project and inputs from the potential end-users (Din Forsyning and TREFOR) has changed the scope of the technology from being implemented at the waterwork to be a container solution to be implemented at polluted well level. It is because the waterworks don’t want contaminated water at their plant if they can avoid it. Besides, the flows are lowest at the individual polluted well level. Therefore, at the end of the MEM2BIO project, it is expected to have a container having all the required facilities including both membrane and biological sand filtration to be sent to the well and treat polluted water for removal of pesticides.

1.6. Research objectives

The research objectives of this thesis are closely related to the tasks of WP1 of the MEM2BIO project. The overall objective of the thesis is:

“How is the performance of membrane filtration with NF, RO, and FO membranes for removal of target pesticides to be combined with biological sand filtration in a pilot-scale water treatment unit?”

To fulfill this objective, the following specific tasks are addressed:

- To Develop analytical HPLC/MS-MS method for the quantification of target pesticides, BAM, MCPA, and MCPP.
- Performance evaluation of candidate NF/RO membranes for pesticides removal and selection of the ideal membrane for removal of target pesticides. The pesticides removal should be >95% at the highest achievable flux.

- Production and delivery of retentates produced by membrane filtration to be treated by biological sand filtration tests for both batch and column experiments. The retentates should be obtained from three groundwater samples from three geographical regions in Denmark, and the ionic composition of produced retentate should be mapped.
- The FO should be studied for removal of target pesticides, and a potential FO membrane should be identified. The FO membrane should be tested for all three groundwater samples.
- To study scaling propensity of RO and FO processes.
- Synthesis of an FO membrane to be used for scaling studies. This membrane should be applicable for both RO and FO processes to be able to make a comparison between two processes in terms of scaling propensity.
- To design a membrane filtration unit for the pilot-scale plant based on the membrane selected in this study.

Chapter 2. Membrane separation for pesticides removal

Membrane filtration has gained an important place in separation processes and is applied in a wide range of applications. Membrane-based filtration for desalination and water treatment have been noticeably employed to address the global concerns of water scarcity and the pollution of aquatic environments. This section provides a general introduction to membrane filtration in particular nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO) processes for removal of pesticides from polluted groundwater.

2.1. Principles of membrane separation

Even though membranes have firstly been used since 1748 by the discovery of osmosis phenomenon, the first membrane developed from lab to full-scale was the first generation of RO membrane for desalination process in the early 1960s [51]. In the past four decades, membranes have been used for a multitude of various applications, especially for seawater desalination, drinking water, and wastewater treatment. Owing to the development of membrane technology, the capital and operating costs of membrane processes have decreased significantly resulting in improved availability, reliability, and efficiency of membranes in different applications, including high-quality water production [51].

Membranes work as selective barriers that can control the permeation rate of chemical components of a mixture through the membrane. For instance, in water treatment, the membrane selectively allows water to permeate freely across the membrane while hindering the permeation of other target impurities such as pesticides [51].

As the most general definition, the membrane can be defined as an interface layer between two neighboring phases, which allows the transfer of matter and energy between the phases with selective or nonselective characteristics [52]. This interface can be symmetric or asymmetric, homogeneous or heterogeneous and porous or nonporous in terms of its structure. It can be solid or liquid and may consist of organic (polymer), inorganic, or biological materials and a combination of them, as well. Membranes consisting of inorganic particles dispersed in the organic bulk are called mixed matrix membranes. Also, membranes consisting of biological species contained in an organic or inorganic matrix are called biohybrid membranes. When membranes are tailored with biocomponents that translate principles from natural biological organisms, they are termed biomimetic membranes. Furthermore, a membrane can be neutral or it can be negatively or positively charged or may consist of functional groups with certain binding or complexing properties. Its thickness can be less than 100 nm up to several millimeters. The term “membrane”, therefore, contains a wide range of various substances and structures, and a membrane might be better to be described by its functionality than its structure or components [52].

In a membrane process, the separation of components of a mixture is based on the difference in transport rates of different species across the membrane. The transport rate of a compound across a membrane is determined by driving forces including pressure, osmotic pressure, concentration, electrical potential, and temperature gradients, as well as by the concentration and mobility of the compound in the bulk of the membrane [52]. The membrane processes and their driving force are listed in Table 2-1.

The pressure-driven membrane processes (PDMPs) are the most prevalent membrane processes used for pesticides removal. PDMPs have the hydraulic pressure gradient as the driving force and in general, are classified according to pore size or molecular weight cut-off (MWCO) into four processes: microfiltration (MF); ultrafiltration (UF); nanofiltration (NF); reverse osmosis (RO) (see Figure 2-1). The MWCO is defined as the molecular weight at which 90% removal is obtained, and is typically used to represent the pore size of membranes. On the other hand, the corresponding membranes for PDMPs are fallen into two categories; porous and non-porous (dense) membranes. A porous structure represents a very simple form of a membrane, that consists of a solid matrix with certain pores with diameters ranging from less than 1 nm to more than 10 mm. The function of porous membranes is determined by pores acting as a sieve to separate the undesired components from the mixture. The dense membranes have no distinct constant pores, but the separation occurs through oscillating free volumes, by solution-diffusion mechanism [51,52].

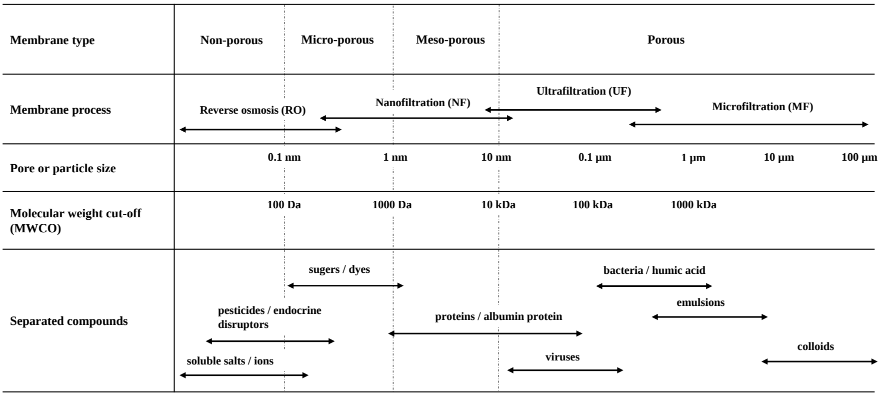


Figure 2-1 The classification of pressure-driven membrane processes.

The removal of a wide variety of organic micropollutants, including pesticides from aqueous solution is usually performed by NF and RO membranes due to the molecular size of pesticides, which is >200 Da. The RO membranes were the first type of membranes used widely commercially, in desalination of water. In RO, hydraulic pressure is applied to overcome the natural osmosis pressure of the aqueous solution to make water molecules and not the other species transport through the membrane to the fresh water. This means that a fairly high operating pressure of 15 to 100 bar is needed to have a sufficient flux in the RO process [53]. Nanofiltration (NF) exists in the form of the transition zone between UF and RO. The "tight" NF membranes function similar to RO where the transport mechanism is dominated with solution-diffusion. The "loose" NF membranes, however, show similarities with UF [53]. The NF, therefor, benefits from low operating pressure compared to RO while still having a high removal for organic compounds compared to UF. Therefore, depending on the NF membrane, the separation in NF is a result of sieving effect in which pores in the membrane sieve out components larger than the pore size of the membrane and/or solution-diffusion, similarly to RO [53].

The performance of NF/RO membranes for micropollutants (e.g., pesticides) is primarily determined by two parameters. The first parameter is the rejection of micropollutants (*R%*) representing the applicability or efficiency of the removal of micropollutants from the water and defined as:

$$\boldsymbol{R}(\%) = \left(\mathbf{1} - \frac{\boldsymbol{C_P}}{\boldsymbol{C_F}}\right) \times \mathbf{100} \qquad \text{Equation 2-1}$$

Where C_p and C_F are the concentration of the solute in permeate and feed, respectively. When the concentration of feed is continuously changed as a result of filtration (e.g., in dead-end mode filtration) the denominator can be corrected as $\frac{C_F+C_C}{2}$ to represent an averaged concentration of feed during the filtration time.

The second parameter to be determined is the water permeate flux of NF/RO membrane, J_w, which is defined as a measure for the rate of filtration:

$$\boldsymbol{J_w} = \frac{\boldsymbol{F_P}}{\boldsymbol{A}} \qquad \text{Equation 2-2}$$

Where F_p is the flow rate of permeate, and A is the surface of the membrane.

An intrinsic phenomenon of all PDMPs is water flux decline throughout filtration, because of concentration polarization and the formation of gel or cake layers by feed solutes rejected by the membrane which is termed membrane "fouling". Fouling compromises the performance of membrane processes and might be caused by the concentration polarization (CP) or adsorption of feed solutes on the surface of the membrane. In membrane separation when a molecular mixture approaches the surface of the membrane, some species (e.g., water in pesticides removal) will permeate through the membrane under a certain driving force, whereas other components (e.g., pesticides) are rejected. Therefore, an accumulation of rejected solutes occurs in the boundary layer neighboring the membrane surface. This phenomenon is termed as concentration polarization (CP). CP takes place in all the membrane processes. Its effects, however, are severely seen in PDMPs. A direct consequence of CP is fouling that leads to a declined flux. Fouling is a general term referred to deposition of organic solutes while biofouling is caused by microorganisms and scaling refers to precipitation of rejected inorganic species on the membrane surface. The handling of CP and fouling/scaling is a challenging engineering aspect of PDMPs [52].

The concentration polarization can be reduced by hydrodynamic measures like adjusting the flow velocity of the feed stream as well as the membrane module design. The handling of fouling, however, is more complicated. The transition from CP to the fouling is explained by “critical flux”. The critical flux is defined as a flux below which flux decline is not observed, while above it fouling occurs. The critical flux is dependent on both membrane and solution characteristics as well as flow conditions [52].

In addition to NF and RO, forward osmosis (FO) has recently received considerable attention for removal of micropollutants. Since FO has also been part of studies in this Ph.D. thesis, it will be subsequently introduced separately in the next section.

2.2. Forward osmosis (FO)

Osmosis is a natural phenomenon that has been harnessed by humans from the beginning of humanity. Ancient cultures noticed that salt could be employed to keep food dried to preserve it for a long time. In high salinity environments, most fungi, bacteria, and other pathogenic microorganisms get dehydrated and die or get inactivated due to the osmosis [42].

Generally, osmosis is defined as the net movement of water through a semipermeable membrane, and the driving force is the osmotic pressure gradient across the membrane. For this reason, the FO is classified as an osmotically-driven membrane process (ODMP). Nowadays, the ODMPs are applicable in a wide variety of applications from food processing and water treatment to power generation (pressure-retarded osmosis process) and novel techniques for drug delivery [42].

In FO, A semipermeable membrane separates two adjacent solutions with a high difference in osmotic pressure ($\Delta\pi$) and allows the passage of water molecules, but retains solutes or ions from one side with lower osmotic pressure to the more saline side. The natural movement of water across the membrane continues until the osmotic pressure on either side of the membrane becomes equal. The highly saline solution with high osmotic pressure is termed as “draw solution (DS)” since it, in fact, draws the water molecules from the other solution which is “food solution (FS).” In the FO membrane process, FS and DS are circulating in either side of an asymmetric membrane while the FS faces the active surface of the membrane and the DS neighbors the support layer of the membrane. Similarly to PDMPs, in FO water flux (J_w) indicates the rate of permeation of water molecules from FS to DS. Simultaneously, depending on the membrane and DS, some of the draw solutes diffuse back through the membrane from DS to FS which is called reverse salt flux (J_{solute}). It is desirable to have a lower J_{solute} value to maintain the osmotic pressure gradient as high as possible.

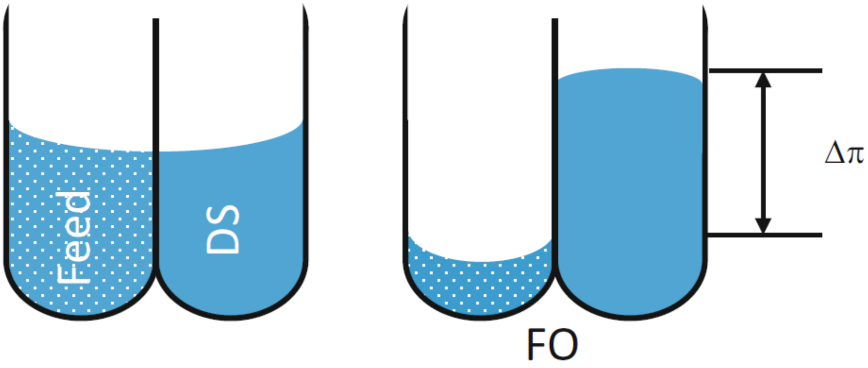


Figure 2-2 The flow of water from Feed to the more saline DS in FO as a result of the osmotic pressure gradient ($\Delta\pi$) [52].

The DS is a highly concentrated solution in the permeate side of the membrane generating the osmotic driving force (Δπ). The DS and its generated osmotic pressures are important parameters affecting the performance of the FO process. Many researchers employed salt as DS, whereas sugars like glucose or ammonia–carbon dioxide solutions have also been used [54]. Lutchmiah et al. have reported that from 2005 to 2013, NaCl was used as the DS in 40 % of the research works due to its low cost, high solubility and generating high osmotic pressure [55]. In the same period, $MgCl_2$ was used in 12% of cases, sugars in 8%, sulfates in 10%, and magnetic nanoparticles in 7% of the cases [55]. Besides, seawater has also been utilized as an attractive candidate for the DS, but its use was primarily influenced by the existence of other microbes and particles in the seawater compromising the performance of FO due to (bio)fouling issue [53].

Similarly to PDMPs, one of the main shortcomings associated with FO is concentration polarization (CP). CP is, however, more severe in the case of the FO process because unlike PDMPs, in FO, there are two types of CPs lowering the water flux (J_w). The asymmetric FO membrane consists of a thin dense active layer and a thicker porous support layer, that increases the complexity of the CP in FO. In FO, the CP occurs in both sides of the membrane. External concentration polarization (ECP) occurs close to the surface of the active layer in feed solution while internal concentration polarization (ICP) takes place inside the porous support layer of the membrane in the DS side. Therefore, the ECP, similar to PDMPs, is described as a concentrative CP whereas the ICP is a dilutive CP diluting the DS. As a result, both ECP and ICP effects lower significantly the bulk osmotic pressure gradient ($\Delta\pi_{bulk}$) to an effective osmotic pressure ($\Delta\pi_{effective}$) and consequently, the water flux (See Figure 2-3).

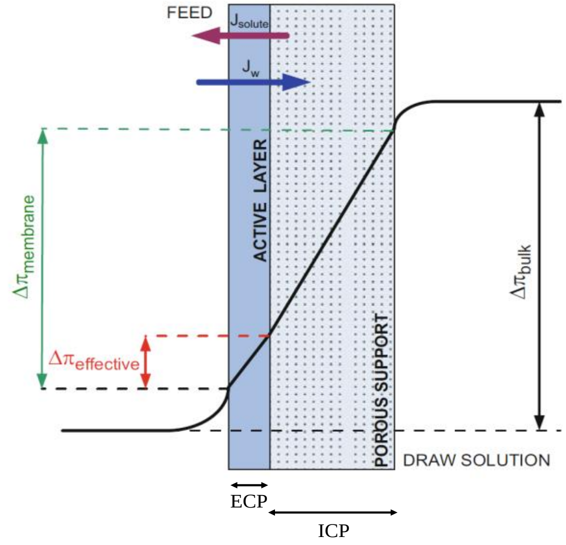


Figure 2-3 The ICP and ECP lower the bulk osmotic pressure gradient to an effective osmotic driving force [52].

In the case of ECP, some hydrodynamic measures such as increasing turbulence through cross-flow velocity can be taken. Moreover, when the membrane is fouled, it is possible to recover the performance of the membrane by osmotic back flush, which is quite straightforward. On the other hand, dealing with ICP is more complicated because it cannot be controlled by hydrodynamic conditions of flow. Alternatively, researchers design FO membranes with minimized thickness and tortuosity of the porous support [56].

Several advantages have also been mentioned for the use of FO in the literature. The most important one is that since FO requires no hydraulic pressures, owing to osmotic pressure generated by DS, it has lower energy consumption than RO, thereby lowing costs, if appropriate draw solutes and their regeneration methods can be technically and economically developed [42,52]. Moreover, it possesses high rejection of a wide range of contaminants, and it may have a lower fouling/scaling propensity compared to PDMPs [42,57]. However, the hypothesis of lower scaling propensity needs to be further investigated as the previous studies used different membranes for RO and FO, and this property was attributed to different membrane materials and not the processes per se [57]. Furthermore, the equipment utilized in FO is simple, and membrane support is less of an issue since the only pressure associated in the FO is a pressure drop in the membrane module. Last but not least, FO is very attractive for pharmaceutical and food processing, mainly because it does not use high pressure or temperature for concertation of the feed, thus does not affect the color, aroma or taste [42,52].

As a result of these merits, researchers pay special attention to FO for several applications such as water/wastewater treatment, seawater desalination [58], nutrients recovery [59], pharmaceutical industry, drug delivery, power generation [60], and drug delivery. FO has been studied for removal of micropollutants, including pesticides that will be discussed accordingly in the next section.

2.3. Pesticides removal by membrane filtration

Nanofiltration and reverse osmosis have been shown as promising treatment techniques for pesticide removal in an effective and reliable way over the last few decades [26,43]. Thin film composite (TFC) membranes have widely been employed in studies to reject pesticides from water streams. TFC membranes are typically used for NF, RO and FO purposes consisting of three layers: an active layer made of polyamide; a porous polysulfone layer and a non-woven fabric backing the membrane. Experimental studies show that the rejection of pesticides varies from excellent using some RO and tight NF membranes to the moderate or poor by some loose NF membranes. According to a review performed by Plakas et al. [26], more than 30 commercially available NF/RO membranes have been employed in experimental tests for the removal of a large variety of pesticides, herbicides, and insecticides in various water matrices. Among these commercial membranes, HR95PP, NF90, NF270, TFC-8821ULP, NTR-729HF, and X20 have relatively demonstrated better results for the rejection of various pesticides [26].

In recent years another type of membranes has been developed functioning between NF and RO membranes requiring lower pressure compared to RO membranes called ultra-low pressure RO membranes (ULRO). The ULRO membranes need relatively lower operating pressure compared to typical RO membranes and at the same time show higher rejection values than the NF membranes. Therefore, the ULRO membranes result in lower operating costs, which are a considerable step to make membrane technology a competitive and cost-effective way for pesticide removal.

Numerous studies have investigated the performance of Dow chemical filmtec XLE membrane which is a ULRO membrane for the elimination of pesticide compounds [61–63]. Surveying those studies, XLE showed satisfactory performance and could be a suitable candidate for the retention of pesticides. Beside XLE membrane, BW30 RO membrane has also demonstrated superb rejection values for several pesticides including BAM which is a locally-remarkable pesticide in Denmark and was one of the target contaminants in this Ph.D. studies [63]. There was not found any study in the literature reporting the performance of commercial XLE, BW30, and NF270 membranes for the rejection of phenoxy acids, MCPA, and MCPP.

There are three primary mechanisms determining the performance of membrane filtration for pesticides removal: steric hindrance (size exclusion), solution-diffusion, and electrostatic interactions (Donnan effects). These transport mechanisms depend on interactions between the membrane and the compounds and consequently, characteristics of both membrane and pesticides to be rejected. The pore size of membrane, as well as the charge and hydrophobicity/hydrophilicity of membrane, are amongst the most important membrane properties. Pesticides characteristics, including molecular size or molecular weight, charge, polarity, and hydrophobicity/hydrophilicity also contribute to the performance of membrane filtration [64–69]. The water matrix also affects the membrane separation through the concentration of pesticides, the ionic strength of the solution, and pH [26].

In general, pesticides can primarily be rejected through either size exclusion or diffusion-controlled mechanisms. If the molecular size of a solute is considerably larger than the pore size or MWCO of the membrane, the steric hindrance (size exclusion) mechanism will be dominant. On the other hand, when the target molecule is in a size range where Van der Vaal’s forces, molecule charge, or other surface interactions can affect the interaction between the molecule and the membrane surface, then diffusion may control the separation. If the solute molecule is too small that no significant interaction with the membrane can occur, then convection will dominate, and no solute rejection will occur [68].

The most dominant transport mechanism for pesticides removal is the steric hindrance or size exclusion or sieving effect. In this mechanism, the relative size of the pesticide molecules to the pore size of the membrane is the most significant parameter governing the rejection of pesticides. This is more pronounced in the case of NF membranes as they can be considered as porous membranes. While some studies showed a positive correlation between the molecular weight (MW) of the species and the rejection [70], it is found that the effect of molecular size is more significant [67]. This is due to the fact that the use of MW does not take into account the spatial geometry of the pesticide molecules, which is important when the length and width of the pesticides deviate significantly.

The concept of spatial geometry effects of micropollutants molecules has led to the development of a number of spherical and non-spherical models for modeling of micropollutants rejection based on steric hindrance mechanism. For instance, some studies have considered molecules as parallelepipeds freely rotating and approaching the pores of the membrane [71,72]. Moreover, in the case of flat molecules when the height is longer than the width of the membrane, it was shown that considering molecules as cylinders give a better fit between the modeled and observed rejection values [73].

The membrane surface characteristics may also influence the rejection of pesticides. The main focus is on the hydrophobicity/hydrophilicity of the membrane surface [74]. Most commercial membranes are thought to be hydrophobic that can be determined by the measurement of the contact angle between the membrane surface and a water droplet. It has been observed that there is a positive correlation between a larger contact angle (more hydrophobicity) with degree of adsorption of a hydrophobic solute on the membrane surface and consequently higher apparent rejection values [64]. Some research attempts also show that the hydrophobic interactions between the membrane and molecules affect the adsorption, but the rejection is not influenced significantly [65,69]. On contrary, the hydrophobicity might have a negative impact on the rejection of solutes as hydrophobic solutes tend to adsorb on the membrane surface, after which they complement diffusion processes of the membrane (known as “breakthrough effect”), resulting in lower rejection values compared to expected values based on size exclusion effect [75]. In conclusion, the hydrophobicity of membrane and solutes, as well as the degree of adsorption, is an important factor that should be subject to investigations in micropollutants removal studies.

Most NF and RO membranes produced for commercial use are negatively charged at neutral pH due to the existence of carboxylic functional groups [15]. The presence of charge bearing groups in the molecular structure of a pesticide might, therefore highly affect the expected rejection, to be higher than expected based on steric model predictions [76]. This can be explained through the electrostatic interactions between the solutes and the membrane surface. Most pesticides remain uncharged at neutral pH, but those containing amine or carboxylic groups dissociate and become charged. Moreover, the charge of a membrane may also affect the rejection of uncharged pesticides through their dipole moment. Van der Bruggen et al. suggested that a high dipole moment can result in a decreased rejection as the polar pesticide oriented itself along the axis of its dipole moment, which lowered the cross-sectional area of the part of the pesticide facing the membrane [67].

The pesticides removal by membrane separation is not only influenced by the membrane and solutes properties also by the feed water composition such as pH, ionic strength, pesticides concentration, and the presence of organic matters [26,62,77]. Often micropollutants removal experiments are performed using simple water matrices like deionized water. However, the ionic content of real waters compared to deionized water is so important to be considered in the rejection determination studies. It has been observed that usually, the rejection is higher in real water matrices than synthetic laboratory-made solutions using deionized water where there is no other ions present [78]. In the investigation of the tangential streaming potential of membranes in solutions with varying ionic content, it has been found that the zeta potential becomes significantly negative with an increased ionic content that can be explained with anion adsorption [79,80]. Anion adsorption overcomes cation adsorption because the hydrated radius is smaller for anions, and as a result, anions are better able to rid themselves of their sphere of hydration [15]. The ions may adsorb in the pores or on the membrane surface where they partially block the pore entrance and thereby lower the effective pore radius. Another effect that has been introduced is that the increase in ionic content decreases the electrical double layer as it is thought to occur for suspended particles. The decrease in the electrical double layer results in a decreased repulsion of the pore walls. Therefore the pores may contract that results in smaller pore size and consequently, higher rejection values [81].

The presence of organic matters in the water is also another factor influencing the rejection, but more complicated as they might have contradictory impacts on the rejection value based on their interaction with the membrane and solutes. For instance, low molecular weight humic matters were found to increase the rejection of triazine pesticides, due to the formation of a complex between humic matters and pesticides increasing the apparent size of the pesticides. Nevertheless, in the same study, a lower rejection was also obtained for one of the triazine/humic compound combinations, indicating the complex interplay [77]. This effect can be stimulated when divalent cations such as calcium exist in the feed water. These cations may also contribute to the formation of complex and thereby enhance the rejection [77].

Apart from the humic matters, the presence of other pesticides or micropollutants may influence the performance of membrane filtration. It has been observed that the removal of individual pesticides is not the same when the feed water contains only a single pesticide solute or multiple pesticides [62]. The type of membrane might also influence this effect. It was observed that for loose NF membranes, the rejection increased, while for tight NF membranes, it decreased. The decrease was explained by competitive adsorption of the pesticide solutes, where the occupation of adsorption sites by one pesticide results in less adsorption and thus higher flux of the other pesticide across the membrane. For the loose NF membrane, it was speculated that the largest pesticide could adsorb in the pores and thereby block the passage of the smaller pesticides [62].

Furthermore, the organic matters may also lead to the fouling of the membrane and therefore change the surface chemistry, that can affect the rejection. If the pesticides tend to dissolve in the fouling layer easily, the impact of the fouling layer may be to increase the concentration of pesticides in the close vicinity of the membrane, and this may result in a decreased rejection due to the diffusion of the accumulated pesticide through the fouling material. On the contrary, if the fouling layer plays as an additional barrier layer for the pesticides to permeate, the rejection might consequently increase [61].

Lastly, the operating conditions such as feed water flow velocity in the cross-flow filtration mode, water flux, and recovery have also been found to be influential in the pesticides rejection. For instance, Chen et al. showed that pesticides rejection increased when high flux and low recovery achieved, whereas the rejection was minimized at high recovery and low flux, which is in line with the solution-diffusion model [68]. This finding is in agreement with another research, where the rejection of both atrazine and dimethoate was observed to be higher when the pressure (water flux) increased from 0.6 to 1.2 MPa [82].

In conclusion, the literature survey shows that pesticides removal by NF and RO membrane processes is a complicated process in which a wide range of parameters from solute and membrane properties to water matrix and operational condition can contribute. It is, therefore, so important to select a proper membrane while other factors are taken into account. Also, most studies are completed at spiked high concentrations which leads to some unknowns that necessitates further elucidation in micropollutant level concentrations.

2.4. Recent advances in RO/FO membranes

Conventional materials and synthesis techniques for membranes are greatly based on empirical methods and control of the structure in the selective layer of the membrane is limited, therefore hindering the performance, and increasing the cost of water treatment. Recent improvements in membranes used in water treatment have not been so effective due to intrinsic constraints of conventional membrane materials such as the trade-off between selectivity and permeability hampering the attainable water-solute selectivity and causing high fouling propensity. Novel materials that can be used in large-scale fabrication and molecular-level design approaches are crucial for overcoming these constraints and for substantially advancing water purification [83]. In this section, recent advances to make membranes used in NF/RO/FO more selective and permeable will be briefly presented. The advances also include the minimization of the fouling propensity of the membranes.

As previously mentioned, the current NF/RO commercial membranes used in micropollutants removal are asymmetric thin film composite (TFC) polyamide membranes. This class of membranes together with cellulose triacetate (CTA) membranes are being produced as commercial FO membranes, as well. In TFC membranes, the thin polyamide layer is a product of interfacial polymerization (IP) of an aqueous solution containing m-Phenylenediamine (MPD) monomer and an organic phase containing 1,3,5-Benzenetricarbonyl chloride (TMC). The IP takes place on the surface of an underlying porous polysulfone (PS) substrate, and a thin layer of polyamide (usually <200 nm) is formed. The most common approach to enhance the characteristics of water purification membranes is through manipulating the IP by introducing new materials into the polyamide layer. Some modifications also target the porous support layer that is performed by manipulating phase inversion (PI) that is a technique to produce the porous PS substrate.

Recently, the development of nanotechnology and nanomaterials (NMs) has opened new routes to the production of nanocomposite membranes, where the term “nano” relates to the internal structure (morphology) of the membrane. In general, nanocomposite membranes are prepared by incorporating NMs (the filler) into the matrix of the polymeric membrane associated with a polymer binder. The NMs may be either dispersed in the polymer solution before membrane synthesis or coated onto the membrane surface [84]. The nanocomposite membranes are classified into three categories: 1- thin film nanocomposite (TFN) membranes in which the NMs are entrapped in the active thin layer of TFC membranes, 2- substrate-coated TFN membranes in which NMs are coated on the top of support layer of TFC membranes, 3- surface-coated TFN membrane, in which NMs are coated onto the top surface of TFC membrane. The nanocomposite membranes are also referred to a general term “mixed matrix membranes (MMMs)” in which inorganic NMs are introduced within the matrix of the membrane [85,86].

The nanocomposite membranes are fabricated to fine-tune the selectivity, permeability, morphology, and physicochemical properties of membranes to increase selectivity by modifying the surface characteristics and morphology, improve the water permeability by increasing the hydrophilicity and enhance antifouling properties by tailoring of the surface chemical properties decreasing the roughness of the membrane [86].

A wide variety of NMs has been used in membrane preparation for different applications including desalination and water treatment. In the most general way, the nanomaterial fillers can be classified into four categories [86]. The main category is the nanoparticles that are subclassified as metal/metal oxides such as Ag [87], TiO_2 [88], Al_2O_3 [88], ZrO_2 [88], SiO_2 [89], ZnO [90], CuO [91], and zeolite [92]; carbon-based nanoparticles like activated carbon and fullerene [93]; and polymeric nanoparticles like polydopamine [94,95]. The second category is the nanofibers that can be organic like cellulose and polyacrylonitrile, and inorganic like titanate [86]. The third class is the nanotubes that carbon nanotubes (CNTs) [96], halloysite nanotubes (HNTs) and biological aquaporin proteins [97] are the most famous materials of this type. The last category is the nanosheets that graphene oxide (GO) has been received special attention from this type [98].

Amongst all the NMs, carbon nanotubes, zeolite, graphene oxide sheets, and aquaporins have received particular attention due to their superior influence on the modification of membranes for different applications [99]. However, aquaporin proteins have been already commercialized for various applications, including FO that is of interest of this Ph.D. thesis. Therefore, a brief description of these membranes will be presented accordingly.

2.4.1. Aquaporin membranes

Aquaporins are the protein channels that control water flux across biological cell membranes. In 2003, Peter Agre won a Nobel Prize for discovering these proteins existing in the cell of all live organisms like animals, plants, bacteria, and archaea. They called it Aquaporin-1, which is also found in human tissues transporting water rapidly through cell membranes. A single aquaporin has a size of 120 kDa, with a tetramer structure consisting of four channels [83,100]

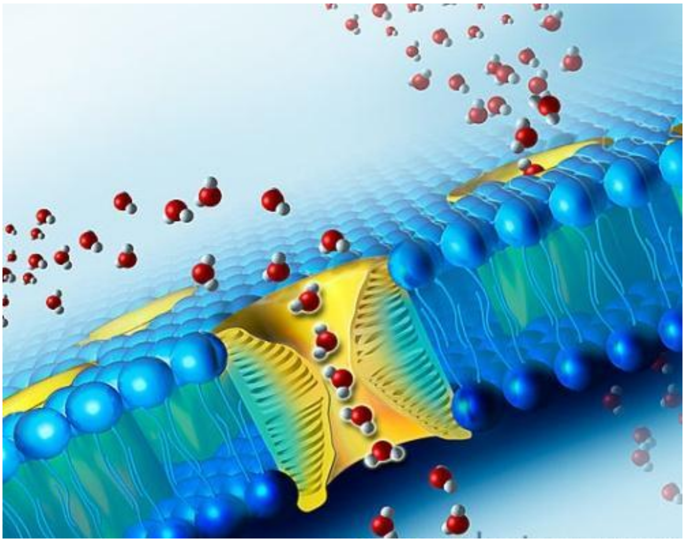


Figure 2-4 Aquaporin protein channels within a cell membrane [101].

These channels are responsible for the physiological plumbing of the organs of our bodies such as kidney, brain, and red blood cells. Water transport mechanism in aquaporin proteins is driven by selective, fast diffusion based on the osmotic pressure gradient. The hourglass shape of AQP1 (See Figure 2-4), with selective extracellular and intracellular vestibules at each end, allows water molecules to pass rapidly in a single-file line, while excluding proteins [100].

The discovery of these aquaporin vesicles led to a significant development in the membrane synthesis by incorporating these water channels into the TFC membranes. The biomimetic aquaporin membranes have potentially higher water permeability without compromising the salt rejection. A single aquaporin channel can conduct 2 to 8×10^9 water molecules per second besides an excellent rejection of ions and other species. It is also stated that 75% coverage of aquaporins provides a hydraulic permeability of approximately 2.5×10^{-11} $ms^{-1}Pa^{-1}$ that is about an order of magnitude more than commercially available RO membranes [100,102].

A Danish company named Aquaporin A/S has incorporated aquaporin proteins into a thin bilayer film supported by a porous substrate. After several years of research, this company has started the commercial production of aquaporin membranes based on its patented technology known as “Aquaporin Inside™”. In this technology, aquaporin proteins are hosted by a thin film coating which ensures that the natural activity of proteins is preserved throughout water purification. This technology has been implemented in both RO and FO membranes that FO membranes are presented in flat-sheet and hollow fiber modules containing aquaporin proteins on the lumen side of fibers [103].

Till now, only a few research groups have investigated the potential of aquaporin membranes in the removal of micropollutants, including pesticides. For instance, Xie et al. employed the aquaporin flat-sheet membrane for the rejection of a total of 30 trace organic contaminants (TrOCs). The TrOCs in their study included uncharged and charged compounds with different hydrophobicity/hydrophilicity properties. It was found in their study that an excellent removal can be achieved with aquaporin FO membrane when a draw solution of 2 M NaCl was used. They also found that the transport mechanism of aquaporin membrane was dominated with solution-diffusion model [104]. In addition, Engelhardt et al. used the first generation of hollow fiber aquaporin prototype to reject three TrOCs. It was found that all three compounds were rejected >99% [105]. Furthermore, the removal of several neutral disinfection byproducts by aquaporin membrane was evaluated in another article and the results were compared with cellulose triacetate (CTA) membrane. It was shown that the aquaporin membrane was capable of rejecting those compounds within the range of 31% to 76% [106].

In particular, for pesticides removal, Madsen and co-workers used aquaporin membrane in a tiny FO lab-scale setup to remove atrazine, BAM and desethyl-desisopropyl-atrazine (DEIA) and compared the results with a CTA FO membrane produced by HTI company. Unlike the rejection values obtained by the CTA membrane, aquaporin membrane showed superior rejection values of >97% for all the target pesticides. As a result, this research served as a baseline for our studies to use aquaporin FO membranes for removal of BAM and Phenoxy acids. Our studies focused on the effect of different lab setups on the obtained results as well as the use of different draw solutes and water recoveries for the removal of pesticides targeted in MEM2BIO.

Chapter 3. Use of NF/RO membranes for the removal of pesticides

This chapter presents the highlights related to the paper I published in Separation and Purification Technology volume 215. This study is closely related to the tasks of WP1 of MEM2BIO project. In general, it was firstly aiming at developing an analytical method for quantification of target pesticides, BAM, MCPA, and MCPP. Furthermore, it aimed at evaluating the performance of candidate NF and RO membranes for pesticides removal and selection of a proper membrane for removal of target pesticides. In particular, this study investigates these research questions:

1- How applicable are candidate commercial NF and RO membranes for removal of pesticides/PTPs and what is the best choice to be used in MEM2BIO groundwater treatment unit?
2- How is the filtration affected by the level of contamination (concentration of pesticides) in the polluted water?
3- How is the filtration affected by the real groundwater matrices in Denmark?
4- Is it possible to reach higher recovery values (80-90%) for membrane filtration? How does it affect the removal of the pesticide?
5- Is the dominant rejection mechanism steric hindrance? Can the rejection of target pesticides be modelled with a simple pore flow model?

3.1. Background

NF and RO are the primary membrane processes that can be employed to treat feed water polluted by pesticides. This is because most prevalent pesticide molecules are within 200-500 Da in size and the MWCO of most commercial RO and tight NF membranes is at the same range. Nevertheless, the MWCO serves as a rule of thumb for membrane selection and as previously discussed the pesticides rejection performance of NF and RO membranes is dependent on several various parameters of the membrane, pesticide molecules, water matrix, and operational conditions. For pesticide transformation products (PTPs), it was previously shown that NF membranes were not capable of pesticides removal at high levels [63]. However, the effect of pesticides concentration on the rejection level of pesticides/PTPs by NF membrane was not subject to the study. Therefore, based on the literature review, two NF membranes, NF270 and NF99HF, an RO membrane, BW30, and an LPRO membrane, XLE were selected to be studied. Although the choice of pesticides in this study was related to the MEM2BIO project, the target pesticides include both charged and uncharged pesticide and PTP. In this way, it was possible to perform a comprehensive study and observe the effect of various membrane/solute properties on the filtration.

Adsorption of the pesticides for the NF/RO membranes was also determined to see to what extent it is an influential parameter. Adsorption might cause overestimation of rejection in the early stages of the filtration [62,107]. Therefore, the actual rejection values were determined using saturated membrane pieces and compared to apparent initial rejections.

To explain the governing rejection mechanism, it was studied whether the removal of the pesticides/PTPs could be predicted with a fairly simple pore flow model, as described by Kiso et al. elsewhere [63,72]. From an engineering perspective, the application of such a model would be very interesting as it would make it possible to anticipate the rejection of a wide variety of pesticides for a given membrane by experimentally determining only a small carefully-selected subset of the pesticides. For this purpose, non-spherical (parallelepiped) geometric parameters of the pesticide molecules need to be calculated using a computational chemistry software, like Gaussian.

Moreover, the majority of pesticides removal tests using membrane filtration has been done with a simple water matrix like demineralized water. In some studies, the influence of the presence of other ions (ionic strength) has also been investigated [62,63,78]. The dominant finding is that by the use of a stronger ionic environment as the feed water, the removal of the pesticide is expected to become higher [63,78]. Some observations, however, did not conform to this hypothesis and showed contradictory impacts depending on the membrane and pesticides used in the investigation [62]. As a result, it was essential to understand the behavior of the membrane filtration with respect to the target pesticides and selected membrane, when real groundwater matrices were used. To do so, three groundwater samples from different regional supply areas in Denmark, Varde, Kolding, and Hvidovre, were used. These locations that were selected based on the Danish monitoring program of pesticides, represent a wide range of ionic strength hardnesses from 6 - 7 ˚dH (German degree) for the Varde water to 25 -30 ˚dH for the Hvidovre water. Also, the impact of recovery as an operating condition on the filtration was part of the study. Since, MEM2BIO aimed at obtaining 80-90% of the flow of feed water as purified water in the membrane unit, the recovery was included in the study.

3.2. Results

As can be seen in Figure 3-1, the RO membrane, BW30, and the LPRO membrane, XLE, were found to reject all three pesticides above the required level (>90%) in MEM2BIO, when a laboratory-level concentration of 1 mg/L was used. In a comparison between BW30 and XLE membrane, even though the observed rejection values for BW30 was ~3% higher than XLE membrane, XLE was a preferable choice as its permeate flux was almost twice that of BW30. The two NF membranes, NF99HF and NF270, showed similar partial rejection values with having the lowest level for the target PTP, BAM (~32%). The rejection of phenoxy acid herbicides, MCPA and

MCPP, were observed to be significantly higher than the BAM for NF membranes, but still lower than needed (66-70% for MCPA and 79-82% for MCPP). The overall difference in the performance of NF with RO/LPRO membranes can be explained with the higher MWCO of NF membranes. However, before finalizing the selection of a proper membrane it was essential to making sure whether this finding was valid in an environmentally relevant concentration.

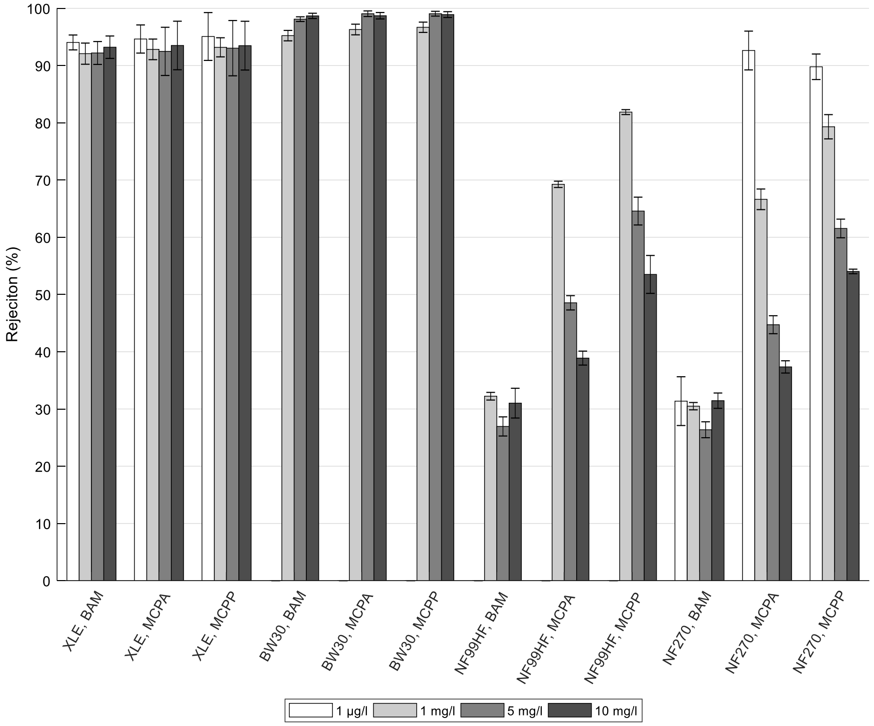


Figure 3-1 The rejection of BAM, MCPA, and MCPP by XLE, BW30, NF99HF, and NF270 at different pesticides concentration determined at 50% recovery and 10 bars. Error bars represent the scatter of data within a 95% confidence interval obtained from triplicate experiments [108].

The most interesting finding of this study was the use of different concentrations for the pesticides in the feed water. It was previously thought that the effect of solute concentration on the rejection behavior of membranes is negligible [62,67,109]. We found, however, that it depends on the governing mechanism of the membrane separation and the properties of both membrane and solutes. In our case, by using lower concentration of 1 µg/L the rejection values significantly increased for charged phenoxy acids and remained almost unchanged for uncharged pesticide, BAM. This suggested that the steric hindrance was not the only descriptor of the rejection mechanism for NF membranes and charge repulsion between negatively charged membranes and phenoxy acids was also contributing in the rejection. By an increase in the concentration of compounds from 1 µg/L to 10 mg/L, the presence of pesticides molecules in the electric double layer increased that might shield the charge of NF membranes surface and diminish the electrostatic repulsion between NF membranes and charged phenoxy acids.

The effect of electrostatic interactions between NF membrane surface and charged phenoxy acids could be revealed from the pore flow model results where the modeled rejections significantly deviated from the observed rejections for NF membranes. In addition, the model was not good enough to give an excellent fit for RO/LPRO membranes. Therefore, one can conclude that the steric model cannot be used to model rejection of a set of pesticides in which charged species are included.

The adsorption of target pesticides was not found to be a great value, and most adsorption (~10-13%) occurred on the RO membranes as they were more hydrophobic and more hydrophobic phenoxy acids tended to adsorb on their surfaces. The reported rejections in this study were quite close to actual rejection values after performing three consecutive filtrations indicating that the adsorption sites were saturated by preconditioning as described in paper I [108].

Eventually, even though the rejection level was considerably higher for phenoxy acids (90-92%) by NF270 in micropollutant concentration level, since the MEM2BIO mainly targets BAM, XLE was selected as the proper membrane for MEM2BIO capable of removing all pesticides at a high level (>92%) while having reasonable permeate flux. Therefore, the rest of the studies was continued with the XLE.

Furthermore, the rejection values were positively affected when real water samples with higher ionic strength were used. It was primarily due to pore blocking effect where the pores of the XLE membrane become clogged with ions present in the groundwater samples. This was aligned with the finding of other researchers [63,67,110] and could be validated with a declined permeate flux for the real matrices. Another evidence on this phenomenon was the estimated pore size for XLE membrane using the pore flow model that showed a decrease as going from lower to higher ionic strength (from Varde to Hvidovre water). It could be partially due to the formation of a complex between dissociated phenoxy acids bearing negative charge in the pH of the solution (pH=5.3) and cations in the solution such as Na^+, Ca^{2+}, and Mg^{2+} resulting in a larger species to be filtered and consequently higher removal rates.

Lastly, the recovery with Varde water also had a positive correlation with the rejection performance of XLE membrane for all the pesticides. The main reason for the increase in rejection with increased recovery from 10%-90% was increased ionic strength, which leads to an increase in rejection through pore-blocking effect as observed in the use of real water samples.

Chapter 4. Combination of the membrane filtration and biodegradation

This chapter presents the highlighted results from the collaborative paper II published in Science of The Total Environment volume 694. This part of the Ph.D. studies was the main part of MEM2BIO project carried out in close collaboration with WP2. In this phase of the project, the selected membrane from the first phase, XLE, was used to produce retentates from three groundwater samples to be used as feed for further biodegradation of BAM by biological sand filters. This was firstly done for batch experiments as presented in paper II as well as column experiments that a paper is under preparation. The batch experiments served as a proof of the novel concept of combination of membrane filtration and biological sand filtration. The focus of this chapter is mainly on the membrane filtration of the combined concept.

In particular, this study sought answers to these research questions:

1- How the composition of water samples collected from different regions changed after undergoing the membrane filtration? Is the concentration of pesticides and nutrients high enough in the retentates to stimulate the biodegradation with bacteria?
2- Can increased concentrations of pesticide and other nutrients in the retentate produced by membrane filtration potentially stimulate degrader activity and support growth to maintain a population of bacteria competent of continuous and effective pollutant degradation?
3- If the membrane filtration is a booster for biodegradation, how much the retentate from membrane filtration needs to be concentrated? In other words, is there a correlation between the recovery of membrane filtration and biodegradation?

4.1. Background

The bioaugmentation of sand filters with some specific bacteria capable of degrading pesticides has been previously studied as a green technique to be implemented in the drinking water treatment plants (DWTPs) [111]. In this way, the DWTPs can be just retrofitted with no need for the addition of chemicals or process to the existing treatment process.

As earlier mentioned, owing to its interesting properties like cell adherence and temporary invasion of native community present in the sand filters, MSH1 has been previously used as a BAM degrader and is thought to be one of the few bacteria capable of using BAM as its sole carbon source even at micropollutant concentrations level [112–114]. However, Albers et al. have previously shown in a pilot-scale bioaugmented sand filters that after 2-3 weeks, MSH1 population lost cell densities and consequently BAM degradation potential [11], with the obtained capacity for BAM removal consequently disappearing within ~2-3 weeks of inoculation. They explained that different reasons might contribute to this issue such as loss of MSH1 as a result of the backwash of sand filters, competition with the native microorganisms already existing in the filters, protozoan predation and starvation due to the low BAM concentrations [11,115]. Another research group also pointed out the starvation of the microorganisms to be the main contributor to the loss of BAM removal capacity after 2-4 weeks when the concentration of BAM in feed water was only 0.2 µg/L [49]. Simply put, the BAM degrader, MSH1, needed more nutrients and a higher concentration of pesticide to survive and keep on degrading BAM in the long-term. Then a preconcentration strategy can be useful to boost the biodegradation.

On the other hand, as previously discussed, membrane filtration is an excellent choice for the removal of pesticides, in particular, BAM, and at the same time produces a retentate stream where the pesticide pollutant and all the minerals and carbon sources become highly concentrated. Membrane filtration has been shown to be a good match for preconcentration of feed for AOPs [33,40,41,46]. Therefore, membrane filtration can be a potential candidate to be combined with biodegradation and provide concentrated feed water for MSH1 (See Figure 4-1).

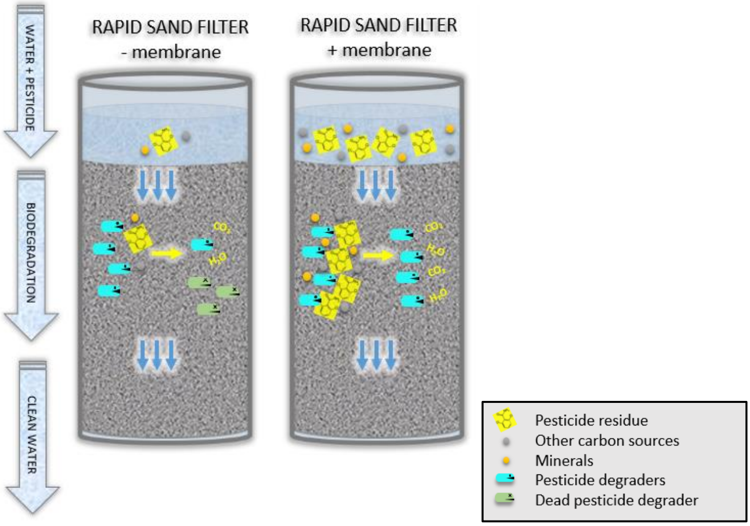


Figure 4-1 An illustration showing inoculated sand filters with and without membrane preconcentration [116].

Similar to the previous study, water samples were collected native water (CNW) from the clean water reservoirs of three waterworks in Varde, Kolding, and Hvidovre. The CNWs were then filtered with XLE membrane in a cross-flow membrane unit to obtain retentates R50, R80 and R90 with permeate recovery levels of 50%, 80%, and 90% which is corresponded to volume reduction factors of 2, 5 and 10, respectively. Then both CNWs and their produced retentates were subject to biodegradation studies in two setups. In the first setup, the water samples were spiked with respective concentrations of ^{14}C-labeled BAM. It was assumed that the concentration of BAM in the CNWs was 0.3 µg/L then the R50, R80, R90 were spiked with 0.6 µg/L, 1.5 µg/L and 3 µg/L, respectively. In the second setup, both CNWs and R90s were spiked with 1.5 µg/L to study the effect of concentration of ions and nutrients at the same pollutant concentration. Afterward, the removal and demineralization of BAM were evaluated using MSH1 in batch experiments for 180 mins.

4.2. Results

In the first step, the composition of CNWs and their respective retentates were mapped to see how the concentration of major ions, trace metals and non-volatile organic compounds (NVOC) in the CNWs changed after being concentrated with membrane filtration.

The mapping of the retentate compositions indicated increased concentrations of NVOC and major ions in higher recoveries, whereas trace metals had a more scattered pattern. Hardness increased significantly from CNW to R80 and R90 retentates, indicating the possibility of scaling when operating at high recovery. Nevertheless, based on the previously reported rejection of major ions by XLE membrane [63], the observed increase in concentrations of the ions was lower than expected. The theoretically expected concentrations of major ions were calculated using PHREEQC software while assuming that there was no accumulation during the filtration, and the retentates were equilibrated with calcium carbonate. A comparison between calculated and measured concentrations displayed that there was a considerable disparity. It was attributed to the ionic adsorption on the surface of the XLE membrane that was validated using a series of followed up experiments. In fact, part of the ions adsorbed on the fresh membrane surface instead of being present in the concentrated retentates.

Although the ionic adsorption to some extent decreased the concentration of retentates, they were adequately and distinctly concentrated on being employed for investigating the hypothesis of booting biodegradation with retentates produced from membrane filtration. It should also be noted that the adsorption would not affect the concentration level of retentate in a real continuous process since the flows are not comparable to the adsorption sites on the membrane surface.

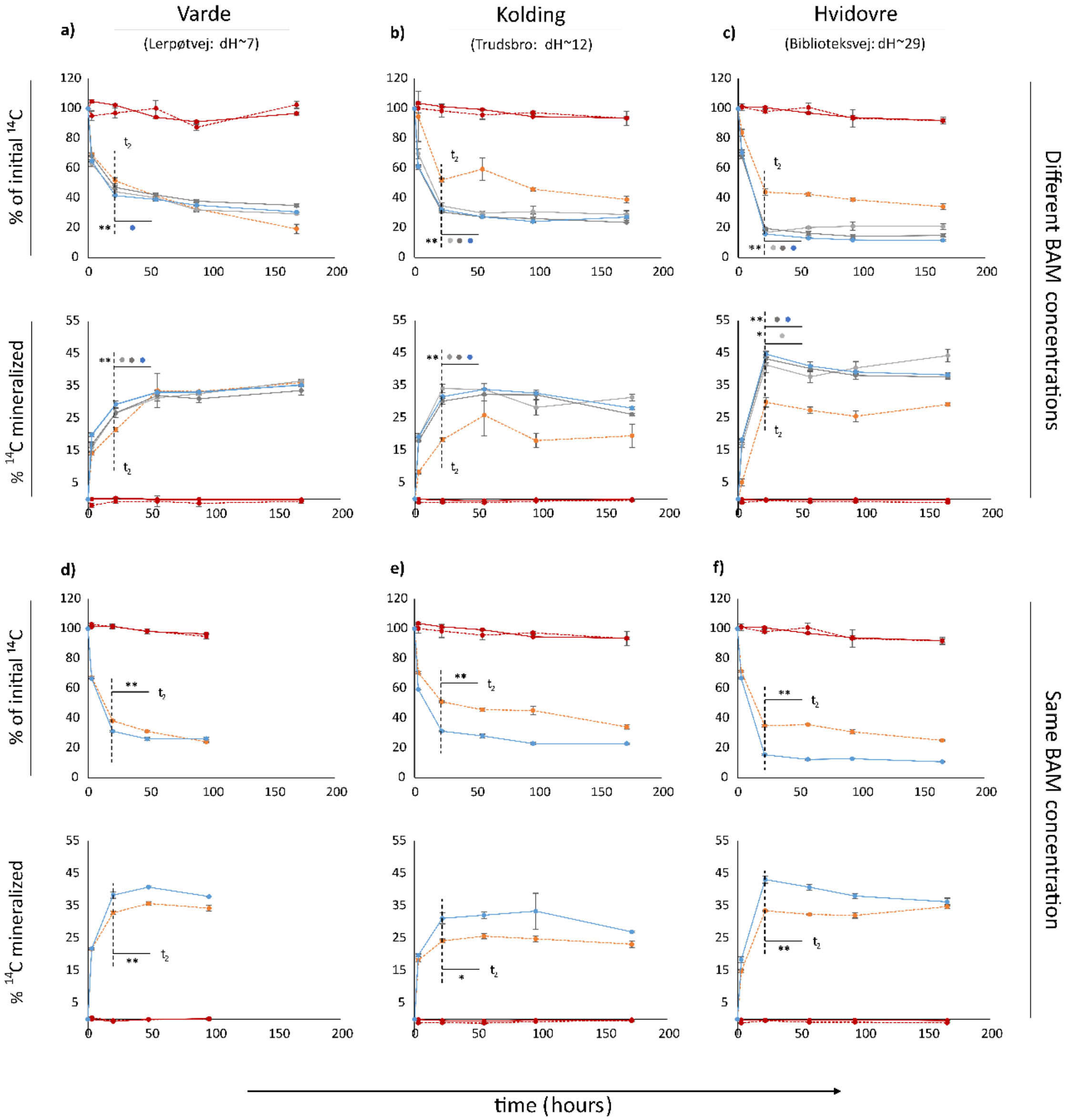


*Figure 4-2 MSH1 BAM removal and mineralization in Varde (left), Kolding (middle) and Hvidovre (right) CNWs and retentates. a – c) MSH1 removal and mineralization over time for treatments with varying BAM concentrations. d – f) show results from treatments with same BAM concentration. Treatments with CNWs are shown as dashed lines and retentates as solid. Treatments with MSH1 inoculation are marked as follows: CNW;0.3 µg/L BAM (•, **orange**), R50; 0.6 µg/L BAM (•, **light gray**), R80; 1.5 µg/L BAM (•, **dark gray**) and R90; 3.0 µg/L BAM (•, **blue**). Treatments without MSH1 (negative controls) are marked (•, **red**). At t_2 (dashed gray line), color legends indicate which treatments differ significantly from CNW. Single asterisk (*); p<0.05 and double asterisk (**); p<0.01 (n=3). Error bars represent standard error of the mean (n=3), where very low errors are indiscernible on plot* [115].

In the next step, the biodegradation batch experiments showed that the potential of MSH1 was stimulated by retentates produced by XLE membrane. This distinctive effect was observed when the retentates from all three locations were compared with their respective CNWs.

As can be seen in Figure 4-2, generally, the degradation activity touched its maximum level within 48-60 hours, and no degradation activity was expectedly seen in the control experiments with no MSH1. The data obtained by the first setup from the Kolding and Hvidovre water samples showed an increased degradation in retentates compared to their respective CNWs (Figure 4-2 b and c), but with no significant variance for different retentates (R50-R90). On the contrary, for the experiment with the Varde water, a greater BAM removal was found for CNW, whereas no appreciable effect was observed in the mineralization between retentates (Figure 4-2 a) [115].

By doing a statistic unpaired student t-test, a considerable effect on mean removal and mineralization values was observed at the first 22 h of experiments. The effect of all retentates compared to CNWs was found to be pronounced for Kolding and Hvidovre waters (all $p \leq 0.01$). For the Varde water, a significant effect on mineralization was observed for all the retentates (all $p<0.01$), while only R90 showed a significantly different effect to CNW ($p< 0.01$) in removal (Figure 4-2 a-c) [115].

The results from the second setup with the same BAM concentration (1.5 µg/L) indicated comparable patterns, with MSH1 BAM degradation touching its maximum in 48-60h and increased BAM removal and mineralization in R90 compared to unconcentrated CNW (Figure 4-2 d-f). In all experiments, the stimulating effect of R90 on both initial removal and mineralization was significant ($p< 0.01$) [115].

The results of the batch experiments demonstrated that concentrating BAM, nutrients, and other water matrix components with XLE membrane improved the degradation potential of MSH1. However, these experiments did not investigate some essential properties like starvation, the survival of MSH1 at a long time, and cell adherence. Therefore, a set of long-term column experiments was also carried out with only DNWs and R90s from the same regions. The experiments were performed in columns containing sand filters inoculated with MSH1 at 10 °C for 40 days. The results of these experiments have not been published yet; therefore, a brief explanation of the experiments and highlighted results will be presented here.

In column experiments, two groups of bench-scale sand filters (columns) were studied for continuous biodegradation of BAM over 40 days. The first group of columns was fed with CNW Varde water while the second group was fed with 10X concentrated R90 retentate. In each group, there was a control column that was not inoculated with MSH1 whereas the other three columns were inoculated with MSH1 BAM degrader bacteria. An illustration and photo of columns are presented in Figure 4-3. The CNW Varde water was spiked with 0.3 µg/L of BAM and the R90 concentrated water was spiked with 3 µg/L of BAM to resemble the up concentration of factor 10 (10X) in membrane treated water. The columns were fed continuously at a flow rate of 4.8 mL/h resulting in a residence time of ~3 hours in the columns.

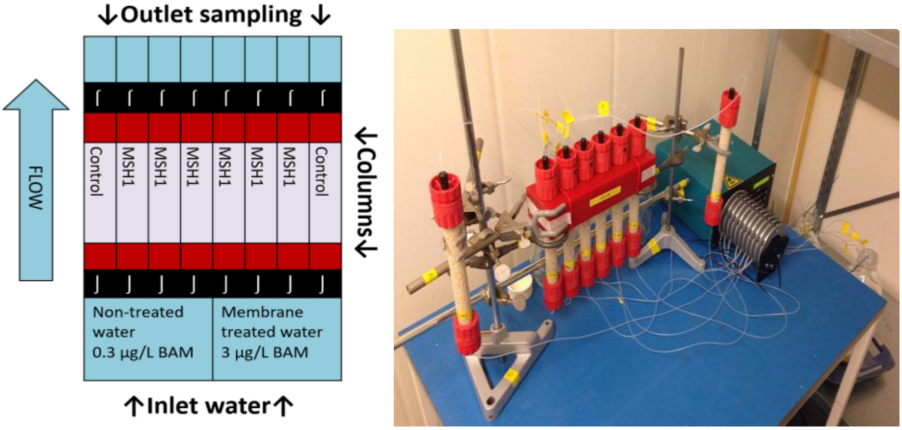


Figure 4-3 Illustration and photo showing the column studies [116].

The BAM removal results for column studies are presented in Figure 4-4. BAM concentrations in the outlet from the inoculated columns were below detection limit throughout the entire experiment. This represents the complete removal of the spiked 3.0 µg/L BAM in the membrane treated water and of the 0.3 µg/L BAM in the untreated inlet water. The two non-inoculated control columns did initially not show any removal of BAM. However a gradual decline in BAM concentration in the outlet water was detected for the control column receiving membrane treated ending with 1.4 µg l^{-1} BAM left in the outlet water. However, study on the number of protozoa showed that the higher number of protozoa in the columns supplied with membrane treated water suggesting a higher microbial growth potential in these columns.

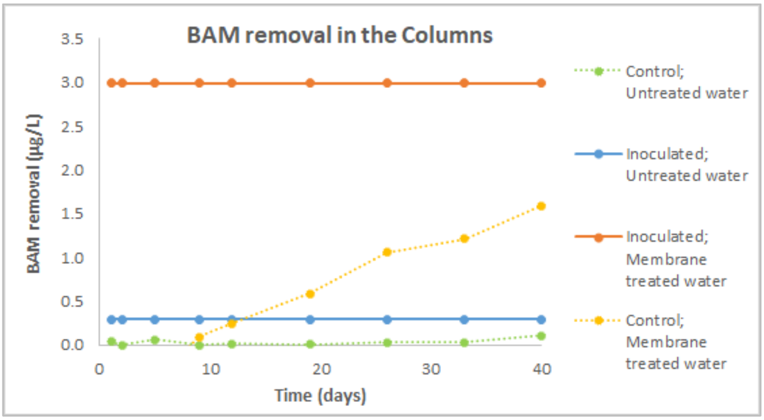


Figure 4-4 Data from column studies compares BAM removal in columns inoculated and uninoculated with MSH1 fed with membrane treated and untreated water samples [116].

Chapter 5. Use of FO for pesticides removal

This chapter concerns the highlighted results of paper III that is under review in Journal of Membrane Science. Some of the information provided in this chapter is also still under manuscript preparation to be submitted as an article. The FO membrane process has been proposed in MEM2BIO project as one of the potential substitutes for the RO in the removal of target pesticides. Therefore, in this part of the study a potential FO membrane, aquaporin membrane, was employed to evaluate the rejection performance of the FO process. The research questions that are answered in this study are as follows:

1- Is the FO process using aquaporin membrane capable of removal of all the target pesticides at high levels?
2- Can aquaporin FO membrane be used for the pilot-scale tests? How is the effect of going from lab-scale to pilot-scale in the early stages of aquaporin membrane?
3- How is the FO rejection affected by the use of a real groundwater sample? How the process behaves when different draw solutes are used?

5.1. Background

The NF and RO/LPRO membranes have previously been studied for removal of pesticides and XLE LPRO membranes showed a superb rejection and permeate flux for removal of both BAM and phenoxy acids. However, owing to its driving force, the emerging FO is known as a process with a low cost of energy and low fouling/scaling propensity compared to pressure-driven membrane processes like NF and RO. In addition, as previously discussed, the presence of more nutrients in the concentrated retentate partly justified the idea of combining membrane with biological filtration in MEM2BIO and in the FO there is back diffusion of draw solute to the feed solution. Then through the use of different draw solutes, it might be possible to tailor the concentrated retentate chemistry sent to biological degradation to provide the retentate with the desired species boosting microbial activity and survival. Therefore, it was a necessity to have a comprehensive study on the FO for the treatment of groundwater polluted with pesticides of concern.

Aquaporin technology, as earlier mentioned, has gained attention due to its superior permeation flux without compromising selectivity, which is a key property for the utilization of the FO process in real applications. In our earlier preliminary study at Aalborg University, the emerging aquaporin FO membrane was tested to reject BAM and two other pesticides. This was done by using a very tiny piece of the first generation of commercialized aquaporin membrane [117]. The rejection of BAM was found to be >97% and a moderate permeation flux of ~7 $Lm^{-2}h^{-1}$was obtained, as well. Nevertheless, the setup used a very small piece of membrane sheet that the obtained results might be varied when moving toward larger scale. On the other hand, the use of a small and simple FO system is a good motive to promote the FO process in separation technology laboratories and expand the development and application of FO membranes. Therefore, the idea was to compare FO setups in different scales to understand whether a very small piece of membrane can be used to accurately estimate the rejection performance of a pilot-scale FO membrane system.

In the first step, it was attempted to use aquaporin membrane in two different setups. The first lab-scale setup was similar to what is used by most researchers in FO studies, while the second setup was a pilot-scale using a hollow fiber membrane. This study enabled us to investigate the impact of the use of different FO setups from a very small piece of membrane in our previous study to the most prevalent lab-scale FO setup and ultimately a pilot-scale hollow fiber module with 2.3 m^2 of effective area.

Furthermore in the second part of FO study that have not been published yet, glucose and sodium acetate were used as draw solutes and the results were compared to sodium chloride as the most commonly used draw solutes. A real water matrix from Varde was used and the performance was evaluated.

5.2. Results

The characterization data of the flat sheet aquaporin membrane showed that the pure water flux in FO mode was 15.54 $Lm^{-2}h^{-1}$, twice our previous study [117] and in line with a newly studied aquaporin membrane [104]. The pure water and salt permeability parameters (A and B), however, were found to be higher than the other studied aquaporin membrane. A was found to be 3.03 $Lm^{-2}h^{-1}bar^{-1}$ and B was 1.76 $Lm^{-2}h^{-1}$ while in other studies the salt permeability was within 0.05-0.09 $Lm^{-2}h^{-1}$ [104,118,119]. The reverse salt flux and salt rejection were also found to be 5.7 $Lm^{-2}h^{-1}$ and 92.8%, respectively that were not again aligned with previous studies. Based on the higher reverse salt flux, A and B, as well as lower salt rejection compared to previously used aquaporin membranes it was speculated that the flat sheet membrane used might be damaged having pinholes or defects. This could also be caused by lot-to-lot variability as there was already another study where the obtained parameters were similar to our study [120], and the authors argued that their used aquaporin membrane was a prototype membrane focusing at having higher flux and not the selectivity.

The rejection data for the flat sheet membrane with the lab-scale FO setup also showed relatively lower than expected values. The experiments were performed using a 1 M NaCl DS and 1 mg/L spiked pesticides in Milli-Q water as the FS for 280 minutes in which the DS was diluted by a factor 2. The rejection of BAM was 93-94% while the phenoxy acids were rejected 95-98% throughout the experiments. The larger molecular size and negative charge of phenoxy acids contributed to the higher rejection compared to the BAM. The lower BAM rejection compared to our previous study [117] might be again due to the presence of defects in the membrane or batch-to-batch disparity. However, it was not possible to redo the experiment with a new batch of flat sheet aquaporin membrane, as the company stopped producing flat membranes and alternatively they have focused on hollow fiber modules.

On the contrary, the hollow fiber membrane illustrated an excellent rejection while maintaining the high pure water flux of 15.55 $Lm^{-2}h^{-1}$. As seen in Figure 5-1, BAM was rejected up to 98.7% while the rejection value was almost 99.2% for MCPA and MCPP. The BAM rejection was comparable with the earlier study by Madsen et al. (97.2%) [117]. The modeling by the solution-diffusion model also showed a good match between the predicted and the observed BAM rejection as it was also shown in the previous study [117].

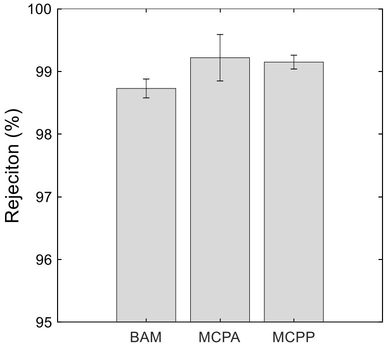


Figure 5-1 The pesticides rejection data obtained by hollow fiber aquaporin membrane. Error bars represent the scatter of data within a 95% confidence interval obtained from triplicate experiments (from Paper III).

In conclusion, a fairly compatible result for BAM rejection could be obtained by any of these three FO systems. This allows us to conclude that the tiny setup used in our previous study can be used for quick, inexpensive and simple rejection evaluation for a wide variety of micropollutants that have not been studied before and in this way a new route can be opened to the application of FO process.

Use of different draw solutes was carried out by the hollow fiber module. As presented in table 5-1, all the pesticides were rejected >98% using three selected DS. However, NaCl showed the highest rejection values as well as the reverse flux, while the glucose had the lowest reverse flux and pesticides rejection.

Among the draw solutes, the NaCl had the smallest molecular size with the highest back diffusion through the membrane from DS to FS while the sodium acetate (pKa=4.54) at the pH of the DS dissociated to large negative acetate ions that were strongly repelled away from the negatively charged surface of aquaporin membrane resulting in the lowest reverse flux. The difference in reverse salt flux can justify the distinct rejection values when using different draw solutes. The higher draw solute reverse flux from DS to FS can hinder forward diffusion of pesticides molecule resulting in increased rejection of pesticides in the case of NaCl [121]. In contrast, the sodium acetate molecules with having the lowest reverse flux would hinder the permeation of pesticides molecules to the less extent as such the rejection value became lower.

Table 5-1 Pesticides rejection data as well as water and draw solute reverse flux using different draw solutes.

Draw solute	**BAM (%)**	**MCPA (%)**	**MCPP (%)**	**Pure water permeate flux ($Lm^{-2}h^{-1}$)**	**Draw solute reverse flux ($gm^{-2}h^{-1}$)**
NaCl (1 M)	98.7	99.2	99.2	15.6 ± 0.8	1.7 ± 0.4
Glucose (2 M)	98.1	98.6	98.9	18.0 ± 1.3	1.1 ± 0.5
CH_3COONa (1.1 M)	97.8	98.2	98.3	12.1± 0.1	0.8 ± 0.6

The use of Varde water as a real groundwater matrix showed that as previously discussed in Chapter 3, the rejection of pesticides is more pronounced when real water with higher ionic strength is applied (See Figure 5-2).

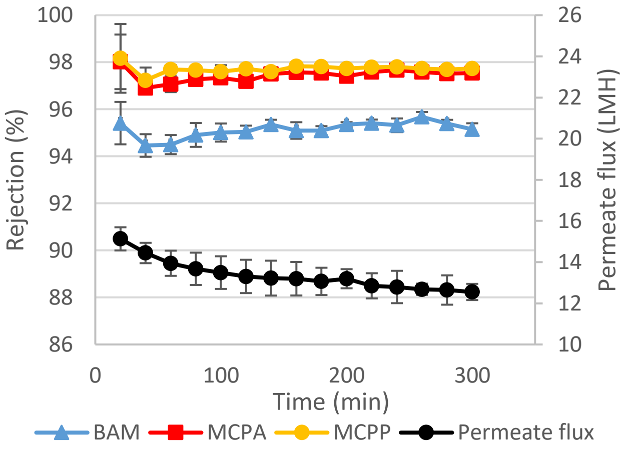


Figure 5-2 The rejection of pesticides and water flux obtained by aquaporin FO membrane with the water sample from Varde. Error bars represent the scatter of data within a 95% confidence interval obtained from triplicate experiments.

Chapter 6. Preparation and scaling analysis of a polydopamine incorporated RO/FO membrane for pesticide removal

This chapter is based on draft manuscript IV. The membrane synthesis was performed at the research group of Professor Bart Van der Bruggen, at KU Leuven, Belgium. The draft manuscript focused on the synthesis, characterization, performance evaluation for pesticides removal and scaling propensity analysis of a membrane that can be used as both RO and FO membranes. This work is primarily beyond the borders of MEM2BIO project and particularly answers this research question:

- Is the FO membrane process less prone to scaling compared to RO when the same membrane material is used?

6.1. Background

As previously mentioned in Chapter 2, the FO process is thought to have less propensity to fouling and scaling compared to RO as it is associated with no hydraulic pressure. Nevertheless, recently, several researchers have reported opposite observations. For instance, it was reported in a study that no difference was observed in the flux decline between RO and FO fouling and it was attributed to a lower initial water flux than the threshold flux [122]. For alginate and silica fouling, it was also observed in a lab-scale study that fouling propensity was the highest for FO compared to membrane distillation and RO [123]. Tow et al. used a method for in situ fouling quantification and found greater foulant accumulation in the FO than the RO, suggesting that alginate fouling in FO might be more severe than RO despite the observed lower flux decline in FO [124]. The emphasis in the MEM2BIO project is, however, on the scaling since groundwater samples mostly contain inorganic content. In a recent study on scaling propensity, Tow et al. showed that flux decline as a result of gypsum scaling started to occur at considerably higher scalant concentrations in the FO than the RO. They used, however, different membrane materials for FO and RO tests and attributed the higher scaling resistance of the FO to the low surface energy of CTA FO membrane [57]. Therefore, for a fair study comparing two processes, the membrane must be of the same material.

The most common RO membranes are TFC membranes with a polyamide active thin layer lying on a porous substrate. The use of commercial TFC membranes (e.g., XLE or BW30) for the FO will result in a very low permeate flux mainly because of a thick support layer stimulating the ICP. In this part of the study, therefore, it was attempted to prepare a TFC membrane applicable for both RO and FO filtration to be able to do the scaling analysis and investigate the hypothesis of having higher scaling propensity for the FO, per se. Mussel-inspired polydopamine (PDA) incorporated membranes have recently gained tremendous research attention in the development of highly permeable and selective TFC membranes for both RO and FO, as PDA tightly adheres to different supports with no structural defect [94,95,125]. The PDA introduces hydrophilic groups such as amine and imine to the active layer of membrane and as such makes the membrane more permeable and hydrophilic. Therefore, it could be a suitable candidate for fabricating highly permeable TFC membrane that can be employed in the FO process, as well. In this study, polydopamine incorporated RO/FO membrane with different MPD/dopamine content was prepared. After characterization and performance evaluation for pesticides removal, the scaling resistance analysis was performed in RO and FO processes.

For the scaling study, calcium sulfate in different concentrations was used as a model scalant, and the initial water flux for both RO and FO processes was set at the same value. The flux decline was used as a measure for scaling propensity and recorded over 24 hours.

6.2. Results

Dopamine was added to the aqueous solution used in the interfacial polymerization containing MPD with a concentration of 0.1 wt.% while the concentration of MPD was set at 1.5, 2, and 2.5 wt.% and the resultant membrane were named TFC-1, TFC-2, and TFC-3, respectively. A control membrane with no dopamine content and 2 wt.% of MPD was also synthesized that was named TFC-0. The SEM images showed that a thin polyamide (PA) layer successfully lied on the porous polysulfone substrate (See Figure 6-1) and by an increase in MPD content, a thicker selective layer was obtained. Also, with increasing DA/MPD ratio, more PDA aggregates were produced, resulting in a higher roughness. The formation of PA could be proven by looking at the FTIR spectrum. Moreover, the presence of PDA was also reflected in the FTIR spectrum through an increase in N–H and O–H stretching vibration resulting in a more hydrophilic surface.

The RO and FO characterization results indicated that the synthesized membrane with 2 wt% of MPD and 0.1 wt% DA (TFC-2) had the optimal performance in terms of permeability and selectivity. Even though the control membrane (TFC-0) with no DA content had a higher salt rejection and rejected pesticides slightly higher in both RO and FO, the TFC-2 showed a superb permeate flux of ~33 LMH in the FO which was

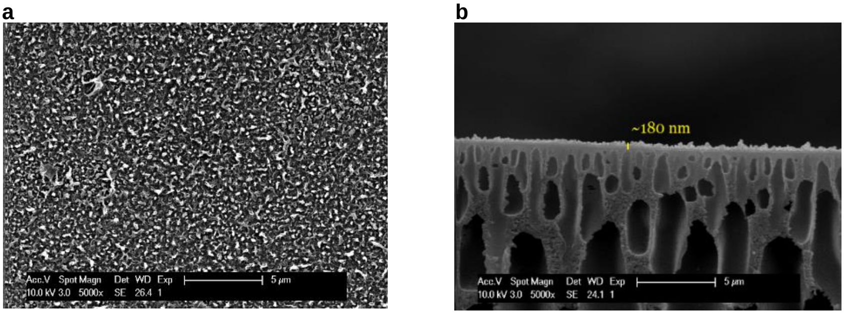


Figure 6-1 SEM analysis shows a) the surface of the synthesized TFC-2 membrane and b) the cross-sectional image of the TFC-2 membrane. The thickness of the thin layer covered on the finger-like polysulfone substrate is almost 180 nm.

Fivefold greater than the control membrane. The TFC-1 membrane with the highest DA/MPD ratio was found to reject salt, as well as pesticides at the lowest level indicating that only 1.5 wt% MPD in aqueous solution cannot form a uniform and tight PA layer in interfacial polymerization. The TFC-3 membrane, with the most MPD content exhibited slightly better salt and pesticides rejection. However, its permeate flux was significantly lower than that of TFC-2. Therefore, TFC-2 was selected as the best membrane giving a satisfactory rejection and a superior permeability for FO applications. This membrane was subject to scaling comparison studies between RO and FO processes.

Table 6-1 The RO and FO performance of synthesized TFC membranes for pesticides removal.

Sample	**R_{salt} (%)**	**FO permeate flux (LMH)**	**Rejection of BAM (%)**		**Rejection of MCPA (%)**		**Rejection of MCPP (%)**		**A** $Lm^2h^{-1}bar^{-1}$	**B** Lm^2h^{-1}	**S** **µm**
			RO	FO	RO	FO	RO	FO			
TFC-0	95.9	7.1	93.3	94.5	94.9	96.1	95.6	96.3	1.16	0.24	1477
TFC-1	43.0	48.8	45.5	28.7	57.8	46.2	63.7	42.4	2.10	11.5	66.3
TFC-2	92.0	33.3	92.8	91.6	93.5	93.7	94.2	94.3	1.56	0.57	125.5
TFC-3	96.6	13.9	94.9	93.7	97.1	95.4	96.8	94.9	1.26	0.17	542.5

Note: TFC-0: 2 wt% MPD, 0 wt% DA; TFC-1: 1.5 wt% MPD, 0.1 wt% DA; TFC-2: 2 wt% MPD, 0 .1 wt% DA; TFC-3: 2.5 wt% MPD, 0.1 wt% DA

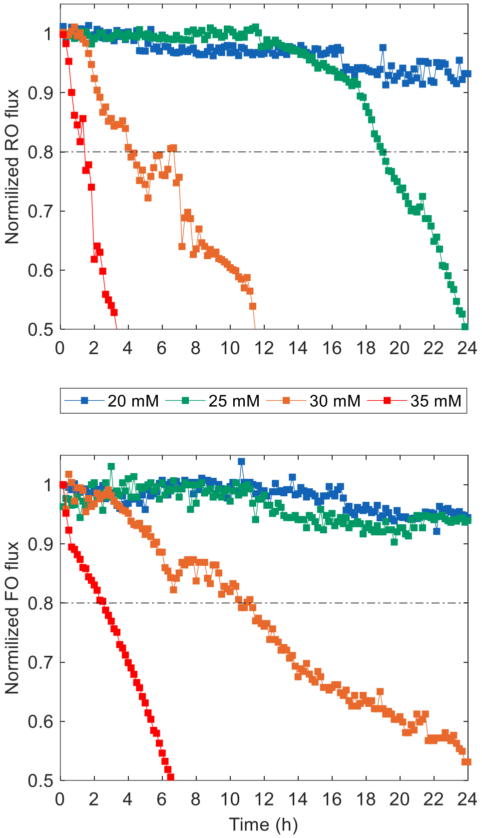


Figure 6-2 Normalized flux decline in RO and FO with different feed concentrations of calcium sulfate. The initial flux was set at 33 LMH in both RO and FO (from Paper IV).

Flux decline measurements for the RO and FO tests that are normalized by initial flux at different gypsum concentrations in the feed water are depicted in Figure 6-2. In RO tests, the flux maintained almost stable for 24 hours at 20 mM of calcium sulfate while at 25 mM a rapid flux decline was observed after a transition period of 18 hours. Tow et al. also observed a delay in flux drop at 24 mM and attributed it to increasing induction time for nucleation of gypsum as saturation index declines toward zero [57]. However, the synthesized TFC-2 membrane could not withstand against 30 mM and 35 mM calcium sulfate solutions and a rapid flux drop was observed within the first hours of experiments. On the other hand, the normalized flux obtained for FO tests showed that no flux decline and consequently scaling occurred in tests with 20 and 25 mM gypsum in the feed solution. The permeate flux started to decline when the gypsum concentration was set at 30 mM and it also rapidly declined at higher concentration of 35 mM. Therefore, it can be concluded that FO process demonstrated a higher resistance toward scaling than the RO, as at 25mM no scaling was observed for FO, whereas the membrane experienced scaling at the same concentration in the RO process. Furthermore, the rate of flux decline at higher concentration of 30mM and 35mM was found to be slightly lower in the FO that might be due to the absence of hydraulic pressure in FO.

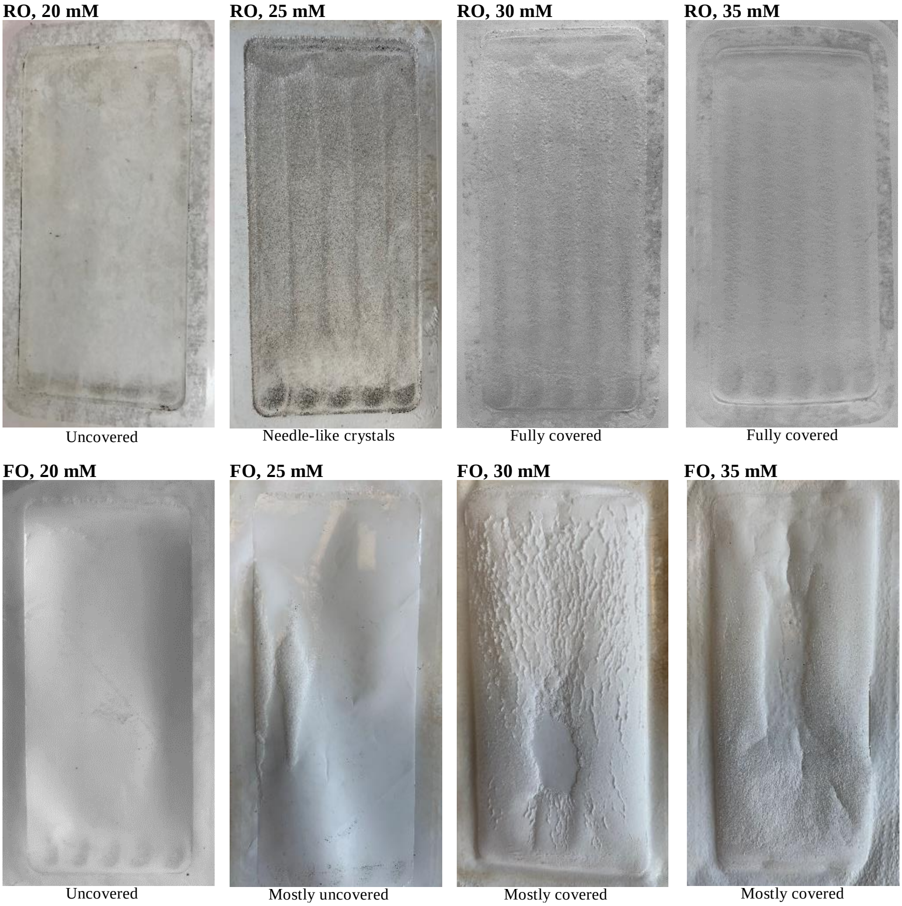


Figure 6-3 Photos showing membranes after RO/FO tests at different gypsum concentrations.

Scaling results obtained from flux decline experiments were examined by visual inspection of the membranes after tests. As can be observed from Figure 6-3, the surface of the membrane in RO maintained almost uncovered at 20 mM concentration except for small crystal growth at the membrane cell channel outlets where the fluid is stagnant. At 25 mM, the membrane in the RO process was found to be covered with needle-like crystals in particular in the flow path. At higher concentrations of 30 mM and 35 mM, where the membrane exhibited a rapid flux decline, the surface of the membranes became fully covered with tightly-attached uniform crystals. In the case of the FO process, at 20 mM the surface of membrane was free of precipitates and at 25 mM crystals covered only part of the membrane surface where the membrane was clamped into the membrane cell. The surface of FO membranes was mostly covered with at 30 mM, and 35 mM and only a small part of the membranes remained free validating the rapid flux drop at these concentrations.

The finding in this study was generally in line with what Tow et al. previously observed [57]. In their study, nevertheless, this difference in scaling resistance between RO and FO was primarily attributed to the difference in membrane material between TFC RO and CTA FO membranes. Here, however, it turned out that the FO process per se is also intrinsically less prone to inorganic fouling (scaling) compared to the RO when the same membrane is used in each processes. In this study, the threshold gypsum concentration for scaling was found to be between 25 mM and 30 mM for FO, while this value was within 20 mM to 25 mM in the case of RO.

Chapter 7. **The pilot study of the MEM2BIO**

This chapter presents a brief description of the pilot plant built as the final product of the MEM2BIO project. The pilot plant was designed as the main task of WP3 based on the results of and in close collaboration with the WP1 and WP2 of the project. As previously mentioned, the pilot plant turned out to be a container solution instead of being implemented in the waterworks. Therefore, a trailer resembling the whole drinking water treatment at waterworks was built by Silhorko-Eurowater A/S company that contains membrane and biofiltration as an add-on to the simple treatment, as well. The aim of the pilot study is to demonstrate a successful removal of BAM and performance of the membrane for a long time (at least three months). This is shown by the removal of BAM to below the threshold limit and 90% recovery of the membranes. The research questions to be answered are as follows:

- Will the introduction of membrane for concentrating BAM and other nutrients (e.g., assimilable organic carbon (AOC)) in the influent water to the biofilters have a beneficial effect on the survival of MHS1 inoculum with prolonged degradation of BAM?
- Will the increase of BAM and AOC change the microbial community in the membrane containing train compared to the non-membrane biofilter? Will MSH1 be relatively more represented in the membrane containing train?

In this chapter, a short description will be presented accordingly.

7.1. Description

The whole idea of the pilot plant is to investigate the possibility of upscaling the lab-scale experiments performed in the MEM2BIO project. This is done by combining the two technologies in one pilot plant located at drinking water well number 130.0590 in central Esbjerg (55°30'28.8"N 8°27'28.9"E). Although the BAM concentration in this water well varies over time, it is averagely 0.3 µg/L which is over the threshold value. The pilot plant is built by Silhorko-Eurowater A/S with an isolating housing. The reason for the isolated housing (See Figure 7-1) is to keep a steady temperature in the pilot plant throughout the operation.

Figure 7-1 An isolated trailer containing pilot plant facilities for MEM2BIO project located by a drinking water well contaminated with BAM in Esbjerg.

As simply illustrated in Figure 7-3, in order to remove residual iron and manganese, the pilot plant consists of an aeration compressor followed by a prefilter before the main treatment trains for pesticide removal; This is the first unit in the pilot plant resembling the simple treatment process in Danish waterworks. From there, the water stream is split into two streams. One flows directly to a sand filter inoculated with MSH1 (Biofilter 2), while the second firstly goes to an ion exchange unit followed by an RO membrane unit and finally to a biofilter with MSH1 (Biofilter 1). The RO unit consisting of two XLE membranes is designed to treat 90% of the flow of the influent water (90% recovery) and produce a factor 10 (10X) concentrate in the remaining

Figure 7-2 Photo showing inside of the pilot plant. The membrane train is shown on the right.

10% retained stream. The concentrate then goes to the biofilter (Biofilter 1) to study the effect of the use of concentrated BAM and other nutrients on the degradation of BAM with MSH1.

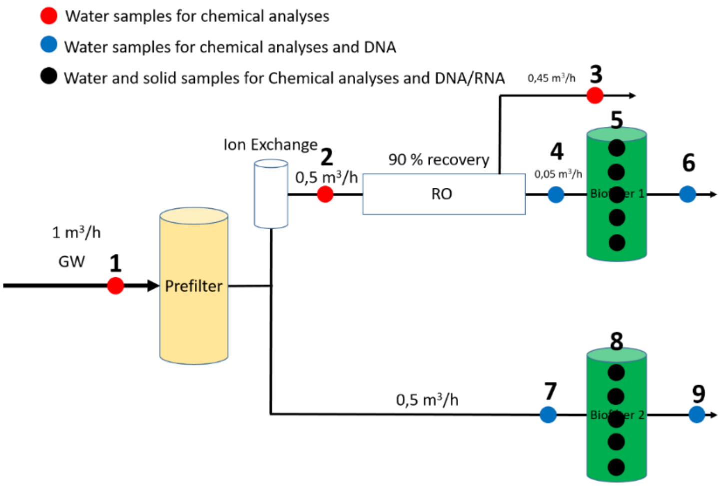


Figure 7-3 Block diagram of the pilot plant showing the sampling spots.

The pilot plant is designed to handle a total inflow of 1 m^3/h of which half flows to the Biofilter 2 and the other half goes to the train with membrane and biofiltration (Biofilter 1). Biofilter 2 serves as a control biofilter where the contaminated feed water is directly led to the biofilter and it can be compared to train 1 with membrane concentration.

For a continuous performance monitoring of the pilot plant, there are a total of seven sampling water taps (marked with red and blue dots in Figure 7-3) and a total of 10 sampling taps from the biofilters (5 from each). The taps located at the biofilter allow us to take water samples for analysis of BAM and water chemistry at different depths.

The pilot plant is intended to run for 6 months from June 2019. Success in the pilot studies is so crucial to ensure this hybrid method can be scaled up and offered as a complete portable solution to be permitted by drinking water authorities in Denmark and throughout Europe, where applicable.

Conclusions

In this study, pesticides and pesticide transformation products have been shown to have a major impact on Danish drinking water production, resulting in many closed wells and delocalization of the drinking water production. The current scheme of aeration and sand filtration is not sufficient to remove the pesticides and degradation products, and therefore, a combined concept of membrane filtration and biological degradation was proposed and investigated as an alternative method for groundwater treatment. Based on the experimental results in this study, it can be concluded that:

- Existing commercial NF membranes can be used to get high removals of pesticides. However, the presence of transformation products in the groundwater can make NF membranes insufficient, requiring the use of more energy-intensive RO membranes that will also demineralize water to a greater extent.
- The simple pore flow model cannot be used for prediction of rejection for a set of pesticides, including charged species. This means that the steric hindrance is not the only descriptor of transport of compounds through NF/RO membranes when both membranes and species are charged.
- The concentration of pesticides in feed does not significantly affect the rejection level of pesticides by membranes. However, in the case of charge solutes and highly charged membranes when the electrostatic interactions also play a role in the separation, the concentration has a considerable impact on membrane performance. Therefore, in order not to dismiss an NF membrane, it is recommended to evaluate membranes in micropollutants level concentrations.
- Rejection values will be higher in groundwater compared to laboratory-grade deionized water because the pore size of the membranes is reduced, most likely due to pore blocking effect. The same effect can increase the apparent rejection when higher recoveries are achieved. In contrary, this will stimulate the fouling/scaling of the membranes and consequently result in flux decline.
- Aquaporin FO membrane also gives high rejection level of pesticides (>98%) while it is associated with increased permeability. The rejection rate is influenced by different draw solutes as well as water matrix.
- Use of various FO systems with different membrane areas shows that a very tiny FO setup can be used to accurately predict the rejection performance of FO membrane in pilot-scale. This finding can promote and facilitate the employment of FO membranes in different applications, including removal of a wider range of micropollutants using a small area of FO membrane in a simple, fast, and inexpensive system.
- Introduction of hydrophilic groups through dopamine into the aqueous phase of interfacial polymerization for the fabrication of TFC membrane can result in an improved permeability in FO application.

- Using the same synthesized TFC membrane, FO process shows a higher resistance toward concentration of a model scalant, namely gypsum compared to the RO filtration. This can be concluded by looking at the permeate flux decline of a membrane in both RO and FO processes.
- Concentrating pesticides (BAM), nutrients, and other real water matrix components with RO membrane (XLE) boosts the degradation potential of pesticide degrading bacteria (MSH1) in batch sand filters. The results are very promising for the development of a novel treatment concept for pesticide polluted groundwater based drinking water and pilot studies are currently running on a contaminated well to study the possibility of scaling up and long-term performance of the proposed hybrid method.

Future perspectives

At the beginning of the Ph.D. studies, a period of 3 years seemed to be long enough to fully investigate all corners and edges relating to this Ph.D. project. However, sitting here at the final stage of the Ph.D., I know that a lot of investigations can be conducted in the future. Some of them include:

- The pore flow model based on the steric hindrance mechanism did not show a satisfying fit between modeled and observed rejection values in this study. There is a necessity for a comprehensive model predicting the rejection of given pesticides with respect to their characteristics. This model should be ideally applicable for any pesticide or in general micropollutants such as charged or uncharged by giving the properties of the used membrane and the compound such as spatial geometry, charge, hydrophilicity, and polarity. Therefore, the inclusion of electrostatic interactions as well as solution-diffusion into pore model or any size-based model would be effective, or it might add unnecessary complexity. It would also be fascinating to include the effect of the ionic environment into the model.
- With respect to the detection of a wide variety of pesticide residues in Danish groundwater, it is recommended to include emerging pesticide residues such as DCP and DMS to the membrane as well as biodegradation studies.
- After completion of pilot studies, economic evaluation of the whole process can facilitate the proposal of this treatment concept to the authorities and the final implementation of this method.
- The whole idea might be beneficial to be considered for the removal of micropollutants in other applications such as wastewater treatment. therefore, it seems to be worth trying for the removal of similar pollutants such as pharmaceuticals, where applicable.
- The scaling propensity study was confined to only one scalant to be comparable with the previous studies with different membrane materials. However, this can be done by using a real water matrix. In addition, this study can include the organic fouling propensity of FO and RO processes using the same membrane material allowing us to make a fair comparison between the two processes.

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