Membrane technology for treatment of surface water in the Mekong Delta
Duy Linh Nguyen

▶ To cite this version:


HAL Id: tel-01759284
https://tel.archives-ouvertes.fr/tel-01759284
Submitted on 5 Apr 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Délivré par l’Université de Montpellier

Préparée au sein de l’école doctorale Sciences Chimiques Balard (ED459)
Et de l’unité de recherche Institut Européen des Membranes (IEM)

Spécialité : Chimie séparative matériaux et procédés

Présentée par Duy Linh NGUYEN

MEMBRANE TECHNOLOGY
FOR TREATMENT OF SURFACE WATER
IN THE MEKONG DELTA

Soutenue le 23 novembre 2016 devant le jury composé de

Mme Murielle RABILLER-BAUDRY, Professeur,
ISCR, Université de Rennes I, France

Président du jury

M. Bart Van Der BRUGGEN, Professeur,
Catholic University of Leuven, Belgium

Rapporteur

M. Sylvain GALIER, Maître de conférences
LGC, Université Toulouse III - Paul Sabatier, France

Rapporteur

M. John PALMERI, Directeur de recherche CNRS,
LCC, Université Montpellier, France

Examinateur

M. André DERATANI, Directeur de recherche CNRS,
IEM, Université Montpellier, France

Directeur de thèse

M. Philippe SISTAT, Maître de conférences
IEM, Université de Montpellier, France

Co-directeur de thèse

M. François ZAVISKA, Maître de conférences
IEM, Université de Montpellier, France

Invité
This thesis was carried out at Department IP2 (Interface, Physic chemistry, Polymer), European Membrane Institute (IEM), Montpellier, France, under support of an excellent team with the participation of many great people who contributed directly and indirectly to this work.

First and foremost, I would like to extend my very deep gratitude to Dr. Andre DERATANI, my main supervisor, who always beside to support as well as encourage by his continuous useful advice and immense knowledge that he shared with me throughout the whole period of three years at IEM. I also place my deep thanks to Dr. Philippe SISTAT as co-supervisor for his precious guidance and scientific assistantship. My special thanks to Dr. Sana Gassara who works like a supervisor and is always willing to help me during the whole thesis.

I also thank to Dr. John PALMERI for his guidance and support to understand of transport phenomena in NF membranes and perform the NF results by Nanoflux® software.

Many thanks go to Mme. Valérie BONNIOL and Mr. Eddy PETIT. I am very grateful for your effort to analyze carefully all my results by HPLC and IC. Working with pilots at the first time can be a challenging task, but I was lucky to have Mme. Loubna KARFANE, Mr. Christophe CHARMETTE, Mr. Jean-Pierre AUDINET and Mr. Bruno NAVARRA who guided and had technical supports to well operate the pilots and get the results presented here.

I would like to show my gratitude to Prof. Marc CRETIN and Mr. Philippe Falque, who help a lot to overcome difficulties at the beginning period and never stops encouraging me by their kindness as well as father-like attitude.

That was actually an interesting gift to meet Dr. François ZAVISKA at the last PhD duration when most of work intended for writing thesis, as well as NF and ED coupling experiments. His comments give assistance to present the coupling experimental results by logical ways and more important to open new development directions for my work in the future.

I wish to express my sincere thanks to the reviewer of this thesis Prof. Bart Van der BRUGGEN and Dr. Sylvain GALIER for their effort to revise this thesis and give out well-founded opinions.
I give my warm thanks to all my colleagues whom I had the pleasure to work with during the realization of PhD. Your help and fruitful scientific discussion that we had together will be precious baggage in my future science work.

Thanks to 911 project via University of Science and Technology of Hanoi (USTH) that financed all of living cost during three years in Montpellier. You give me a wonderful chance to effectuate my dream about doing research at a beautiful developed country, France.

The last but not the least, great thankfulness are sent to my family, my dear friends for their love and unconditional motivation throughout good and bad times. All my love and gratitude.
Access to clean water is one of the most important problems that is encountered worldwide even in countries as water-rich. For instance, the Mekong Delta (MD)’s coastal provinces have to face up to alternated flooding and drought periods. Moreover, climate changes inducing less rainfall and salt water intrusion water severely affect the water quality of the area. The main sources of pollution come from the human and farming wastes including fish, livestock and poultry. Pesticide pollution can also be a serious problem in some areas. The deterioration of water quality in the MD and the lack of access to clean water via safe supply systems in the rural communes entail an increase of waterborne diseases related to the salinity, the presence of microorganism and organic pollutants. The study is aimed at investigating the membrane technology to treat surface water in the MD region in order to produce good drinking water. The study was focused on brackish waters containing pesticides. Two synthetic model water samples were chosen as representative of surface waters found in the Mekong Delta. Desalination and pollutant removal were performed using nanofiltration (NF) integrated with electrodialysis. The Nanoflux® software was used to explain the experimental performance of two NF membranes (NF90 and 270). On the other hand, energy consumption of the two coupled processes was also estimated depending on the quality of water feed. All the data obtained should be used in the future to design a demonstrator pilot for the family-sized production of drinking water.

Keywords: Membrane technology, water treatment, desalination, pesticide, electrodialysis, nanofiltration.
Contents

Acknowledgements ........................................................................................................................................ i
Abstract ................................................................................................................................................ iii
Contents .................................................................................................................................................. iv
List of tables .......................................................................................................................................... x
List of figures ......................................................................................................................................... xi
List of symbols ...................................................................................................................................... xv
General introduction ............................................................................................................................ 1
1 Literature review .................................................................................................................................. 4
   1.1 Mekong Delta .................................................................................................................................... 4
      1.1.1 Administrative overview ........................................................................................................... 4
      1.1.2 River system ................................................................................................................................ 5
      1.1.3 The role of surface water source .................................................................................................. 6
      1.1.4 Some threats towards surface water resource ............................................................................. 7
         1.1.4.1 Climate change ....................................................................................................................... 7
         1.1.4.2 Flooding .................................................................................................................................. 10
         1.1.4.3 Impacts of human activity on surface water source ................................................................. 11
      1.1.5 Surface water quality .............................................................................................................. 12
         1.1.5.1 Salts ....................................................................................................................................... 15
         1.1.5.2 Physical-chemical parameters ................................................................................................. 15
         1.1.5.3 Nutrients ............................................................................................................................... 17
         1.1.5.4 Microbial indicator bacteria ................................................................................................... 17
         1.1.5.5 Metals ................................................................................................................................. 18
         1.1.5.6 Pesticides ............................................................................................................................. 19
         1.1.5.7 Target of treatment ................................................................................................................. 20
1.2 Nanofiltration ................................................................. 21
  1.2.1 Introduction .......................................................... 21
  1.2.2 Application .......................................................... 23
  1.2.3 Transport through the membrane ............................ 24
    1.2.3.1 Exclusion mechanisms .................................... 24
    1.2.3.2 Modeling models of transport ......................... 24
    1.2.3.3 Nanoflux® ..................................................... 29
  1.2.4 Membrane module and process design .................... 31
    1.2.4.1 Membrane module ......................................... 31
    1.2.4.2 Process design .............................................. 32
1.3 Electrodialysis ............................................................ 34
  1.3.1 Principle of electrodialysis ....................................... 34
  1.3.2 Application of ED in desalination ............................ 35
  1.3.3 Factors affecting the performance of ED in desalination 36
  1.3.4 Transport in ion-exchange membrane ....................... 38
    1.3.4.1 Donnan equilibrium ...................................... 38
    1.3.4.2 The Nernst–Planck equation ......................... 39
    1.3.4.3 Transport number ......................................... 39
  1.3.5 Membrane process ................................................ 40
    1.3.5.1 Process parameters ...................................... 40
    1.3.5.2 Concentration polarization in ED .................... 42
  1.3.6 Energy consumption in electrodialysis ...................... 46
2 Salt Rejection performance of NF270 membrane ................. 48
  2.1 Introduction ............................................................ 48
  2.2 Materials and methods ............................................. 48
    2.2.1 Equipment and filtration protocol ....................... 48
vi

Contents

2.2.1.1 Experimental apparatus ................................................................. 48
2.2.1.2 Membrane conditioning ................................................................. 49
2.2.1.3 Filtration experiment ................................................................. 50
2.2.2 Membrane NF270 ............................................................................ 50
2.2.2.1 Contact angle ............................................................................. 51
2.2.2.2 Zeta potential ............................................................................. 51
2.2.2.3 Pure water permeability ................................................................. 52
2.2.3 Salt solutions .................................................................................... 52
2.2.4 Analytical methods ........................................................................ 53
2.3 Results and discussion ....................................................................... 54
2.3.1 Membrane characterization .............................................................. 54
2.3.2 Effect of applied pressure on salt rejections and permeate fluxes .......... 56
2.3.3 Effect of pH on salt rejections and permeate fluxes ............................. 60
2.3.4 Effect of feed concentration on permeate fluxes and salt rejections .......... 63
2.4 Conclusions ...................................................................................... 66
3 Removal of pesticides used in the Mekong Delta by nanofiltration .......... 69
3.1 Introduction ....................................................................................... 69
3.2 Materials and methods ....................................................................... 70
3.2.1 Membrane selection and characterization ........................................ 70
3.2.2 Target pesticides ........................................................................... 71
3.2.3 Synthetic Mekong river waters ........................................................ 72
3.2.4 Analytical methods ....................................................................... 73
3.2.5 Sorption studies ............................................................................. 74
3.2.5.1 Sorption experiment protocol ..................................................... 74
3.2.5.2 Effect of time on the adsorption ................................................. 74
3.2.5.3 Adsorption isotherm .................................................................. 74

vi
3.2.6  Equipment and filtration protocol ................................................................. 75
  3.2.6.1  Experimental apparatus ........................................................................... 75
  3.2.6.2  Separation experiment protocol ............................................................... 75
3.3  Results and discussion .................................................................................... 76
  3.3.1  Target pesticide properties ........................................................................ 76
  3.3.2  Adsorption of pesticides on NF membrane ................................................ 78
    3.3.2.1  Adsorption kinetics ............................................................................... 78
    3.3.2.2  Amount of pesticide adsorbed ............................................................ 78
    3.3.2.3  Absorption isotherm ............................................................................ 80
  3.3.3  Rejection of pesticides in pure water solution ........................................... 83
    3.3.3.1  Rejection of single solution ................................................................. 83
    3.3.3.2  Effect of trans-membrane pressure .................................................... 85
    3.3.3.3  Effect of coexisting pesticides ............................................................. 86
  3.3.4  Rejection of pesticides in synthetic representative river water .................. 87
  3.3.5  Modeling the pesticide rejection by using the Nanoflux® software .......... 90
3.4  Conclusion ....................................................................................................... 92
4  Desalination by electrodialysis ......................................................................... 94
  4.1  Introduction .................................................................................................... 94
  4.2  Materials and methods .................................................................................. 95
    4.2.1  Experiment equipment and membranes ................................................. 95
    4.2.2  Electrodialysis experiment ..................................................................... 96
    4.2.3  Test solutions .......................................................................................... 97
    4.2.4  Analytical methods ............................................................................... 98
    4.2.5  Data evaluation method ......................................................................... 98
  4.3  Results and discussion .................................................................................. 100
    4.3.1  Factors effect to NaCl removal by electrodialysis .................................. 100
4.3.1.1 Effect of concentration ................................................................. 100
4.3.1.2 Effect of applied voltage ............................................................... 101
4.3.1.3 Effect of divalent cations ............................................................. 104
4.3.2 Desalination the permeate solution of NF by ED ............................... 107
  4.3.2.1 Effect of voltage ........................................................................ 107
  4.3.2.2 Effect of flow rate ...................................................................... 109
4.3.3 Desalination the simulated river water by electrodialysis .................. 112
4.4 Conclusion .......................................................................................... 113

5 Nanofiltration and electrodialysis coupling ............................................. 115
5.1 Introduction .......................................................................................... 115
5.2 Materials and methods .......................................................................... 116
  5.2.1 ED – NF integrated membrane process ........................................... 116
    5.2.1.1 ED stage .................................................................................. 117
    5.2.1.2 NF stage ................................................................................ 117
  5.2.2 Optimizing the NF process ............................................................... 118
5.3 Results and discussion .......................................................................... 118
  5.3.1 ED – NF integrated membrane process ........................................... 118
    5.3.1.1 ED performance .................................................................... 118
    5.3.1.2 NF performance .................................................................... 120
    5.3.1.3 Water product quality ............................................................ 121
  5.3.2 Comparison between membrane processes ...................................... 122
  5.3.3 Optimizing the NF process ............................................................... 126
    5.3.3.1 Effect of recovery on permeate flux ........................................ 126
    5.3.3.2 Effect of recovery on the NF efficiency and energy consumption 127
5.4 Conclusion .......................................................................................... 134

6 Conclusion ............................................................................................. 136
Contents

Reference ...................................................................................................................................... 140
Appendix ...................................................................................................................................... 151
Résumé ......................................................................................................................................... 155
List of tables

Table 1-1: Results of the environmental monitoring in Mekong Delta from 3/2012 - 11/2012 [36] ........................................................................................................................................................ 14
Table 1-2: The concentration of heavy metals in Mekong Delta from 3/2012 - 11/2012 [36] ...... 18
Table 1-3: Comparison of properties between NF, RO and UF [4] ............................................... 22
Table 2-1: Bulk Diffusion Coefficients and Stokes-Einstein and Pauling Radii of ions [98]. ...... 52
Table 2-2: Calibration curves for measurement of salt concentrations from ion conductivity ...... 53
Table 2-3: The normalized membrane charge density (ξ) and the effective membrane thickness (L_{eff}) for each membrane – salt pair are calculated by Nanoflux® simulation ............................... 58
Table 2-4: The osmotic pressure and ionic strength of salt solutions in different concentration .. 64
Table 3-1: The characteristics of the membrane used in this study ............................................... 71
Table 3-2: Composition of the synthetic water samples used in the experiment studying the influence of coexisting inorganic salts .................................................................................................... 72
Table 3-3: The MS quantification parameter and the detection limit of the pesticides used ....... 73
Table 3-4: The molecular structure and physicochemical properties of the target pesticides ...... 77
Table 3-5: Comparison of Langmuir and Freundlich adsorption isotherm models ....................... 81
Table 3-6: Ion rejection (%) results in the absence and presence of pesticides and pure water flux increase after each experiment ....................................................................................................... 89
Table 3-7: The summary result of the pesticide rejection modeling by the Nanoflux® software .. 91
Table 4-1: The characteristics of the PCA membranes ................................................................. 96
Table 4-2: The composition of the permeates in NF processes ..................................................... 97
Table 5-1: Concentration of ions in water product of the two integration processes ................ 122
Table 5-2: Rejection performance and energy consumption to treat two simulated river waters by different coupling of NF and ED .................................................................................................. 124
Table 5-3: The ion concentration in the permeate of the Med50 filtration experiment ............... 131
Table 5-4: The ion concentration in the permeate of the Max50 filtration experiment .......... 132
List of figures

Figure 1-1: The Mekong River Basin [10].......................................................................................... 4
Figure 1-2: Maps of river systems and canal networks in the MD [10]............................................. 5
Figure 1-3: Mean lower low waters ($Z_{\text{min}}$) at Tan Chau Station and Chau Doc Station from 1985 to 2015................................................................................................................................. 9
Figure 1-4: Effects of drought and saltwater intrusion production on residents .............................. 10
Figure 1-5: Severe floods at Tan Chau district [26].......................................................................... 11
Figure 1-6: Map of sampling points in Tien River and Hau River [36].............................................. 13
Figure 1-7: Schematic drawing of dead-end mode and mode cross-flow of operation ................. 32
Figure 1-8: Schematic drawing of some cross-flow operations: (a) co-current; (b) cross-flow; (c) counter-current; (d) perfect mixing. .................................................................................................................. 33
Figure 1-9: Process configuration for single pass system and recirculation system ..................... 33
Figure 1-10: Principle of electrodialysis process [63] .................................................................... 35
Figure 1-11: Resistances which apply in a cell pair........................................................................ 41
Figure 1-12: Concentration profiles of the cations in the boundary layer at the surface of a cation exchange membrane during ED process ................................................................................. 43
Figure 1-13: Schematic drawing of a R (= U/I) versus the reciprocal current................................. 46
Figure 2-1. Schematic diagram of the NF pilot.................................................................................. 49
Figure 2-2: The photo of a water drop on the NF270 membrane surface ....................................... 54
Figure 2-3: Zeta potential of the NF270 membrane as the function of pH...................................... 55
Figure 2-4: The plot of the pure water flux as the function of applied pressure ................................ 55
Figure 2-5: The rejection of salt solutions as the function of applied pressure at pH 6................. 56
Figure 2-6: The rejection of the four salts as a function of the permeate flux for NF270 at concentration of 10^{-2} mol/L at pH 6 (Nanoflux® simulation uses $L_p = 15.8 \text{ L/m}^2\cdot\text{h}$, $kires = 1$ and $r_p = 0.535 \text{ nm}$)................................................................................................................. 58
Figure 2-7: The permeate flux of salt solutions as the function of applied pressure at pH 6 ......... 59
Figure 2-8: The permeate flux as the function of trans-membrane pressure at pH 6 of salt solutions: a) NaCl, b)Na$_2$SO$_4$, c) CaCl$_2$, d) MgSO$_4$. Nanoflux® simulation (data experiment): solid blue (star), pure water; solid black (square), salt solution.............................................................. 60
Figure 2-9: The effect of pH on rejections of cations (a) and anions (b) by NF270 (10^{-2} mol/L and 5 bar) ............................................................................................................................................... 61
Figure 2-10: The effect of pH on the permeate flux for different salt solutions (10-2 mol/L and 5 bar) ................................................................................................................................................. 62
Figure 2-11: Effects of feed concentration on the permeate flux for different salts (a) NaCl, (b) Na₂SO₄, (c) CaCl₂ and (d) MgSO₄ (pH 6) ............................................................................................................................................. 64
Figure 2-12: Effects of feed concentration on salt rejections: (a) NaCl, (b) Na₂SO₄, (c) CaCl₂ and (d) MgSO₄ (pH 6)........................................................................................................................... 65
Figure 3-1: Adsorption kinetics of the three studied pesticides on NF270 (a) and NF90 (b) ........ 78
Figure 3-2: Adsorbed amount of pesticides on NF membranes from single solute system and from mixtures (Fen: fenobucarb; Iso: isoprothiolane; Pre: pretilachlor) ................................................ 79
Figure 3-3: Plot of the pesticides loading on the membrane against the pesticide equilibrium concentration in the liquid phase.................................................................................................................. 80
Figure 3-4: The pesticide adsorbed amount as a function of logK_{ow} ......................................... 83
Figure 3-5: Rejection of the pesticides in single solution using NF 270 and NF90 membranes with the following operating conditions fenobucarb (Fen) and isoprothiolane (Iso) concentration = 300 µg/L – pretilachlor (Pre) concentration = 1000 µg/L, pressure 11 bar, the number upper columns is the permeate flux (L/m²h)) ............................................................................................................................................. 84
Figure 3-6: Pesticide rejection at different pressures applied in the case of (a) NF270 and (b) NF90 membranes. ............................................................................................................................................... 85
Figure 3-7: The permeate flux of pesticide solutions at different pressures applied in the case of the (a) NF270 and (b) NF90 membranes. ............................................................................................................................................... 86
Figure 3-8: Rejection of pesticides from single solution and mixed solutions at a pressure 11 bar by (a) NF270 and (b) NF90 membrane (the number upper columns is the permeate flux (L/m²h)) ................................................................................................................................................... 87
Figure 3-9: Pesticides rejection by (a) NF270 and (b) NF90 membrane ....................................... 88
Figure 4-1: Schematic of the batch recirculation mode ED system used in this study .................. 95
Figure 4-2: The ratio of the diluate conductivity as a function of time for different feed concentration at 5V ............................................................................................................................................. 100
Figure 4-3: The kinetic constant and the energy consumpion of the desalination process as a function of feed concentration................................................................................................................. 101
Figure 4-4: Effect of the applied voltage on the ED process for different feed concentrations (a) 0.05 mol/L, (b) 0.1 mol/L, (c) 0.25 mol/L ............................................................................................................................................... 102
Figure 4-5: The rate constant of the desalination process as a function of applied voltage........... 103
Figure 4-6: The energy consumption of the desalination process as a function of applied voltage ......................................................................................................................................................104

Figure 4-7: The ratio of the diluate conductivity as a function of time for different concentration of (a) Ca\(^{2+}\) and (b) Mg\(^{2+}\) in 0.1 mol/L NaCl solution.........................................................................................................................105

Figure 4-8: The rate constant of the desalination process in different feed solution composition ......................................................................................................................................................106

Figure 4-9: Effect of the applied voltage on the ED process for different NF permeate waters: (a) permeate 1, (b) permeate 2 and (c) permeate 3 ..........................................................................................................................108

Figure 4-10: The rate constant of the desalination process as a function of the applied voltage.109

Figure 4-11: Effect of the flow rate on the ED process at 15 V for different NF permeate waters: (a) permeate 1, (b) permeate 2 and (c) permeate 3 ..................................................................................................................110

Figure 4-12: The rate constant of the desalination process as a function of the flow rate .........111

Figure 4-13: The energy consumption of the desalination process as a function of the flow rate ......................................................................................................................................................112

Figure 4-14: The ratio of the diluate conductivity as a function of time for different simulated samples ........................................................................................................................................113

Figure 5-1: The schematic diagram of the coupled process with the maximum and median concentration solutions ........................................................................................................................................116

Figure 5-2: The reduction of conductivity and ion concentration in (a) the median (b) the maximum ED diluate as a function of time ........................................................................................................119

Figure 5-3: The rejection of ions and pesticides by NF process with NF270 of the median solution in comparison between with or without ED pretreatment stage ..............................................120

Figure 5-4: The rejection of ions and pesticides by NF process with NF90 of the maximum solution in comparison between with or without ED pretreatment stage. ..............................................121

Figure 5-5: The experimental permeate flux of the two feed solutions as a function of recovery ......................................................................................................................................................127

Figure 5-6: The energy consumption and conductivity of the feed and permeate as a function of recovery for a) the Med50 and b) Max50 ........................................................................................................................................128

Figure 5-7: The rejection of ions as a function of recovery for a) the Med50 and b) Max50......129

Figure 5-8: The energy consumption and concentration of Cl\(^-\) and Na\(^+\) ion in the permeate as a function of recovery for a) the Med50 and b) Max50 ........................................................................................................................................130
Figure 5-9: The rejection of pesticides as a function of recovery for a) the Med50 and b) Max50

......................................................................................................................................................133
# List of symbols

**Latin letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>effective membrane area</td>
<td>m²</td>
</tr>
<tr>
<td>aᵢ</td>
<td>activity of i</td>
<td>-</td>
</tr>
<tr>
<td>Cᵢ</td>
<td>concentration of i in bulk solution</td>
<td>mol/m³ or (mol/L)</td>
</tr>
<tr>
<td>cᵢₘ</td>
<td>concentration of i in the membrane</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Dᵢ</td>
<td>diffusion coefficient of i in bulk solution</td>
<td>m².s⁻¹</td>
</tr>
<tr>
<td>Dᵢₘ</td>
<td>diffusion coefficient of i in membrane</td>
<td>m².s⁻¹</td>
</tr>
<tr>
<td>dₜw</td>
<td>density of water at 25°C</td>
<td>g/L</td>
</tr>
<tr>
<td>E</td>
<td>electric field strength</td>
<td>-</td>
</tr>
<tr>
<td>Eₜₙes</td>
<td>energy consumption for a desalination process</td>
<td>KWh.m⁻³</td>
</tr>
<tr>
<td>Eₚₚ</td>
<td>energy consumption for a pump</td>
<td>KWh.m⁻³</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
<td>-</td>
</tr>
<tr>
<td>i</td>
<td>electric current</td>
<td>A</td>
</tr>
<tr>
<td>i</td>
<td>current density</td>
<td>A.m⁻²</td>
</tr>
<tr>
<td>iₜₚₘ</td>
<td>limiting current density</td>
<td>A.m⁻²</td>
</tr>
<tr>
<td>Jᵢ</td>
<td>molar flux density of i</td>
<td>mol⁻¹.m⁻².s⁻¹</td>
</tr>
<tr>
<td>Jᵥₜ</td>
<td>volume flux density</td>
<td>L.h⁻¹.m⁻²</td>
</tr>
<tr>
<td>kᵢ₂f</td>
<td>Donnan co-ion partition coefficient</td>
<td>-</td>
</tr>
<tr>
<td>kᵣᵢₜ</td>
<td>Boltzmann constant</td>
<td>J.K⁻¹</td>
</tr>
<tr>
<td>kᵢₕ</td>
<td>partition coefficient of i</td>
<td>-</td>
</tr>
<tr>
<td>Kᵢₜₑ</td>
<td>convective hindrance factors of i</td>
<td>-</td>
</tr>
<tr>
<td>Kᵢₜₙᵈ</td>
<td>diffusive hindrance factors of i</td>
<td>-</td>
</tr>
<tr>
<td>kᵢ⁵ₙres</td>
<td>residual partition coefficient</td>
<td>-</td>
</tr>
<tr>
<td>lₚeff</td>
<td>effective active NF membrane layer thickness</td>
<td>μm</td>
</tr>
<tr>
<td>Lₚₜ</td>
<td>effective water permeability</td>
<td>L.h⁻¹.m⁻².bar⁻¹</td>
</tr>
<tr>
<td>Lₚᵢₜ</td>
<td>pure water permeability coefficient</td>
<td>L.h⁻¹.m⁻².bar⁻¹</td>
</tr>
<tr>
<td>m</td>
<td>weight of permeate solution</td>
<td>g</td>
</tr>
<tr>
<td>N</td>
<td>number of cell pairs</td>
<td>-</td>
</tr>
<tr>
<td>nₚₜ</td>
<td>number of pores</td>
<td>-</td>
</tr>
<tr>
<td>ΔPₜ</td>
<td>pressure difference</td>
<td>bar</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>$\Delta P_e$</td>
<td>effective pressure difference</td>
<td>bar</td>
</tr>
<tr>
<td>$Q$</td>
<td>flow rate</td>
<td>$m^3/h$</td>
</tr>
<tr>
<td>$R$</td>
<td>ideal gas constant</td>
<td>$J.mol^{-1}.K^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>Rejection</td>
<td>none or %</td>
</tr>
<tr>
<td>$R_{am}$</td>
<td>resistance of the anion exchange membrane</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_{cc}$</td>
<td>resistance of the concentrate compartment</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_{cm}$</td>
<td>resistance of the cation exchange membrane</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_{cp}$</td>
<td>resistance of a cell pair</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_{dc}$</td>
<td>resistance of the diluate compartment</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_e$</td>
<td>resistance of the electrode</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$r_i$</td>
<td>ion radius</td>
<td>nm</td>
</tr>
<tr>
<td>$r_p$</td>
<td>pore radius</td>
<td>nm</td>
</tr>
<tr>
<td>$R_{st}$</td>
<td>apparent resistance of the total membrane stack</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T$</td>
<td>limiting transmission coefficient</td>
<td>-</td>
</tr>
<tr>
<td>$t$</td>
<td>operating time</td>
<td>h</td>
</tr>
<tr>
<td>$t_i$</td>
<td>transport number of $i$</td>
<td>-</td>
</tr>
<tr>
<td>$U$</td>
<td>electric potential difference</td>
<td>V</td>
</tr>
<tr>
<td>$V$</td>
<td>solution velocity vector</td>
<td>m/s</td>
</tr>
<tr>
<td>$x$, $\Delta x$</td>
<td>thickness of the membrane</td>
<td>m</td>
</tr>
<tr>
<td>$X_m$</td>
<td>effective membrane charge density</td>
<td>mol/l</td>
</tr>
<tr>
<td>$z_i$</td>
<td>electrochemical valence of $i$</td>
<td>-</td>
</tr>
</tbody>
</table>

**Subscripts and Superscripts**

1 counter ion
2 co-ion
b bulk
bl boundary layer
c concentrate
d diluate
e electrode
### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>f</td>
<td>feed</td>
</tr>
<tr>
<td>i</td>
<td>(i_{th}) component</td>
</tr>
<tr>
<td>m</td>
<td>membrane</td>
</tr>
<tr>
<td>mig</td>
<td>migration</td>
</tr>
<tr>
<td>p</td>
<td>permeate or pore</td>
</tr>
<tr>
<td>s</td>
<td>solute or salt</td>
</tr>
<tr>
<td>S</td>
<td>Stokes</td>
</tr>
</tbody>
</table>

### Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_{im})</td>
<td>effective activity coefficient of (i) in the membrane</td>
</tr>
<tr>
<td>(\mu_i)</td>
<td>chemical potential of (i)</td>
</tr>
<tr>
<td>(\mu_i^\circ)</td>
<td>chemical potential in a given standard state</td>
</tr>
<tr>
<td>(\delta)</td>
<td>thickness of the boundary layer</td>
</tr>
<tr>
<td>(\Delta\Pi)</td>
<td>osmotic pressure difference across the membrane</td>
</tr>
<tr>
<td>(\Delta\varphi_D)</td>
<td>Donnan potential</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>surface porosity</td>
</tr>
<tr>
<td>(\zeta)</td>
<td>current utilization</td>
</tr>
<tr>
<td>(\eta)</td>
<td>current efficiency or pump efficiency</td>
</tr>
<tr>
<td>(\hat{\eta})</td>
<td>dynamic viscosity</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>electro-viscosity coefficient</td>
</tr>
<tr>
<td>(\xi)</td>
<td>normalized membrane charge density</td>
</tr>
<tr>
<td>(\rho(x))</td>
<td>local ion charge density of the membrane</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>osmotic reflection coefficient or conductivity</td>
</tr>
<tr>
<td>(\tau)</td>
<td>pore tortuosity</td>
</tr>
<tr>
<td>(\upsilon_i)</td>
<td>stoichiometric coefficient of (i)</td>
</tr>
<tr>
<td>(\varphi)</td>
<td>electric potential in membrane</td>
</tr>
<tr>
<td>(\Phi_i)</td>
<td>steric hindrance partition coefficient of (i)</td>
</tr>
</tbody>
</table>

### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>ASS</td>
<td>Acid sulfate soils</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological oxygen demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DI</td>
<td>deionized</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>EC</td>
<td>European Commission</td>
</tr>
<tr>
<td>ED</td>
<td>Electrosialysis</td>
</tr>
<tr>
<td>ENP</td>
<td>Extended Nernst–Planck</td>
</tr>
<tr>
<td>ES</td>
<td>steric-hindrance model</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>Fen</td>
<td>Fenobucarb</td>
</tr>
<tr>
<td>GCE</td>
<td>good co-ion exclusion</td>
</tr>
<tr>
<td>GDP</td>
<td>gross domestic product</td>
</tr>
<tr>
<td>HET</td>
<td>hindered electro transport model</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>Iso</td>
<td>Isoprothiolane</td>
</tr>
<tr>
<td>LC</td>
<td>liquid chromatography</td>
</tr>
<tr>
<td>MD</td>
<td>Mekong Delta</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MOH</td>
<td>Ministry of Health of Viet Nam</td>
</tr>
<tr>
<td>MONRE</td>
<td>Ministry of National Resource and Environment of Viet Nam</td>
</tr>
<tr>
<td>MRM</td>
<td>multiple reaction monitoring</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>MSF</td>
<td>Multistage flash distillation</td>
</tr>
<tr>
<td>MWCO</td>
<td>Molecular weight cut off</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>Pre</td>
<td>Pretilachlor</td>
</tr>
<tr>
<td>QCVN</td>
<td>National technical regulation</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SEC</td>
<td>specific energy consumption</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solids</td>
</tr>
<tr>
<td>TFC</td>
<td>thin film composite</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>THM</td>
<td>trihalomethane</td>
</tr>
<tr>
<td>TMS</td>
<td>Teorell-Meyer-Sievers model</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solids</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>VND</td>
<td>Vietnam Dong</td>
</tr>
<tr>
<td>WCA</td>
<td>water contact angle</td>
</tr>
<tr>
<td>WRI</td>
<td>World Resources Institute</td>
</tr>
</tbody>
</table>
Chapter 0

General introduction
General introduction

Access to clean water is one of the most important problems that is encountered worldwide even in water-rich countries. For instance, the Mekong Delta (MD) owns abundant surface water source with a relatively high density network of rivers and canals. However, this region has to face up to alternating flooding and drought periods and climate change inducing less rainfall and salt water intrusion severely affects the water quality of the area. Moreover, the main sources of pollution come from human waste and waste from the fish, livestock and poultry farming. Pesticide pollution can also be a serious problem in some areas. Thus, water quality required for domestic and human drinking purposes is not guaranteed by a direct delivery. To meet the requirements of water quality, surface water must be treated by an effective process that should remain in accordance with water production cost. These two key issues need to be addressed urgently.

In general, rural people have traditional habits for using water, like containing water in large tanks, using aluminum for flocculation and subsequent boiling before drinking. This treatment can remove suspended particles, iron and microbial contamination, but it is not likely to reduce salinity and pesticide residues. For instance, all of six samples taken from household tanks after flocculating in Thoai Son in June 2012 were contaminated by pesticides, exceeding the European Commission (EC) drinking water guideline values for total pesticides [1]. Toan et al. [2] pointed out that the pesticides were detected in the samples of boiled aluminum-treated water taken from surface water by households. The concentration of some of them even increases because of the boiling step.

Regarding the water supply stations, the treatment process is more technical. Firstly, a chemical treatment step with aluminum is applied to surface water to remove suspended particles. After that it is treated by rock and sand filters in combination with disinfection (chlorine). Finally, the treated water is generally stored in water towers from where it is distributed to the connected households. However, the survey of Wilbers [3] revealed that this treatment was inefficient on Cl\(^{-}\) levels since the Cl\(^{-}\) concentration in piped-water is similar to that in untreated surface water. Until now, there has not been any announcement about the residue of pesticides in piped-water. Although some stations have applied treatment technology through filtering by active coal to remove organic compounds, it is very difficult to eliminate completely these pollutants from surface water, due to the lack of good operation and maintenance.
Moreover, water production costs are also a great obstacle to access to clean water for rural people. For example, the percentage of households using piped-water for domestic and drinking purposes is very low, accounting around 28.47 % in the survey of Wilbers et al. [3] for the rural areas of Can Tho, Hau Giang, and Soc Trang Provinces. The reason for this problem not only comes from water quality, but also financial reasons. Particularly, 10.53 % of households with possible access to piped-water prefer not to connect to the water supply station because of high water delivery cost. The connection fees in the rural areas is around 1,000,000 VND (ca. 40 EUR in 2016), while reported monthly earnings of households is just 500,000–5,000,000 VND (ca. 20 – 200 EUR in 2016). The other households (61%) had no possible access to piped-water, since a water supply station was not present or was not operational. Therefore, poor people cannot use piped-water and are forced to utilize other water sources with very low quality, such as rainwater or groundwater.

To solve these problems, we propose applying membrane technology to treat surface water in the MD. Membrane technologies provide effective and lasting solutions for adequate supplies of water of suitable quality to meet human, environmental and industrial needs. There are two basic types of membrane separation processes; pressure-driven and electrically-driven [4].

Pressure-driven technologies include, in order of decreasing permeability: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF and UF often serve to remove large organic molecules, large colloidal particles, and microorganisms. MF performs as a porous barrier to reduce turbidity and some types of colloidal suspensions. UF offers higher removals than MF, but operates at higher pressures. In wastewater reclamation, MF or UF might provide a suitable level of treatment. In drinking water treatment, MF or UF might be used in tandem with NF or RO to remove coarser material so that fouling of the less permeable membranes is minimized [4]. The most commonly used process for the production of drinking water is RO, but NF is now emerging as a viable alternative to conventional water treatment because it can operate at lower pressures and higher recovery rates than RO systems. NF is also cost effective in many groundwater softening applications where the incoming turbidity is low [5].

However, in desalinating saline water, such as sea water and brackish water, containing mainly sodium chloride, there is a problem when NF is employed. NF enables achieving greater than 90% removal of divalent and polyvalent ionic species from aqueous solution, but can
achieve only up to about 70% rejection of monovalent species from the aqueous solution [6], [7]. Consequently, NF must be combined with other membrane processes that differ from the energy intensive RO. Electrodialysis (ED), a kind of electrically-driven membrane process was proposed. ED is known as being more energy efficient than RO for low to moderate salt concentration removal from a feed stream [5], [8], [9].

The objectives of this study are as follows.

1. Study NF and ED membrane technologies to treat brackish water containing pesticides.
2. Quantify the performances of NF and ED coupling to treat synthetic model water samples representative of surface waters found in the MD.
3. Design a demonstrator pilot to apply in a rural area for family-sized application with an assessment of energy consumption and water production cost.

Study plan

To attain the above objectives, the following topics were investigated:

- Overview of the current state of affairs relating to surface water pollution and using water resources in the MD. From that, determination of synthetic water sample compositions to be treated in the laboratory and description of the membrane technology selected (Chapter 1)
- Removal by NF of salt solutions (Chapter 2)
- Removal by NF of pesticides used in the MD (Chapter 3)
- Desalination by ED of brackish waters representative of surface waters found in the MD (Chapter 4)
- NF and ED coupling to treat synthetic model water samples representative of surface water found in the MD with the purpose of a demonstrator pilot design (Chapter 5)
Chapter 1

Literature review
1 Literature review

1.1 Mekong Delta

1.1.1 Administrative overview

The Mekong River flows from the Tibetan Plateau in China to the East Sea, passing through six countries on its way: China, Myanmar, Laos, Thailand, Cambodia and Viet Nam. The Mekong Delta (MD) in southern Viet Nam is the lower part of Mekong River Basin (Figure 1-1). It was formed by the deposition of sediments from the Mekong River over thousands of years. It is the biggest delta of Viet Nam and includes 13 cities and provinces of Long An, Tien Giang, Dong Thap, Vinh Long, Tra Vinh, Can Tho, Hau Giang, Soc Trang, Ben Tre, An Giang, Kien Giang, Bac Lieu and Ca Mau. The total natural area comprises approximately 39734 km². The MD borders on Cambodia in the North, East Sea in the East, Gulf of Thailand in the West and Ho Chi Minh City in the North-West.

Figure 1-1: The Mekong River Basin [10]
The MD consists of flat terrain, mostly of average height of 0.7 to 1.2 m above sea level. The highest place of the delta is along the Cambodian border, from 2.0 to 4.0 m above sea level. Then the relief is lower to the central plains, from 1.0 to 1.5 m high, and only 0.3 to 0.7 m in the tidal and coastal areas [11].

1.1.2 River system

The Mekong River courses into the MD via the Cambodian border by two major distributaries: the Mekong River (or Tien River) and the Bassac River (or Hau River). Both these rivers are splitted into nine branches that form the shape of the MD before running into the East Sea. The MD has a relatively high density network of rivers and canals including natural river systems as well as manmade canals (Figure 1-2).

Figure 1-2: Maps of river systems and canal networks in the MD [10]
Rivers and canals in the MD are classified to three orders: the primary canals, the secondary canals and the third order waterways which are major canals and rivers. The primary canals are mostly artificial canals and are used for irrigation and water discharge from agricultural fields. The flow velocity of the primary canals is very low in the rain season about 0 to 1 m$^3$/s. They are even dry during the dry season. The secondary canals are the connection between their primary canals and main canals or rivers to discharge water. The flow velocity of the secondary canals is around 1–15 m$^3$/s. Some of them in coastal regions are significantly higher (up to 30 m$^3$/s) because of effects of the tidal regime. The total length of the primary canals and the secondary canals is more than 50,000 km [12], which ten times higher than the entire length of the Mekong River. The third order waterways include major canals and rivers which water flow ranges from 400 to 6000 m$^3$/s.

The two main distributaries, Tien River and Hau River, transfer a large amount of water yearly with a total flow about of 325 km$^3$/s observed at Tan Chau station (on the Tien river) and 82 km$^3$/s in Chau Doc station (on the Hau river) [11]. This surface water is the main water resource in the MD.

1.1.3 The role of surface water source

Surface water resource plays an important role in the socio economic development of the MD. It is not only the main factor for agricultural production, but also as a motivation for industrial development. At the same time, surface water is also the main source for human activities, including drinking water.

Today, the mainstay economy at the MD is agriculture with nearly 70% of the delta’s population relying on rice production for their livelihoods [13]. This is the biggest rice production region in Vietnam holding about 25 million tons of rice annually for domestic consumption as well as export. It is often referred to as Viet Nam’s ‘rice bowl’. The total paddy planting area is about 4.34 million ha in which 98% is irrigated by surface water [14]. In addition, the surface water resource is also indispensable to the aquaculture and the orchard plantings.

Industry in the Mekong Delta has been developing in recent years. There are 74 industrial zones and 214 industrial parks with a total area of about 32 thousand ha. In that regard, the major industries include agro-processing and fishery processing. According to the report of the Mekong River Commission, the industrial activities use about 24% of total water withdrawals in the MD [15]. Surface water appears then one of essential factor to impulse the development of industry in this region.
For the domestic purposes like cleaning, washing, cooking or drinking, different water sources are used including surface water, groundwater, rainwater, and piped-water, etc. The piped water corresponds to clean water from the water supply stations. The water source providing for these stations comes from 90% of surface water and 10% of groundwater. To improve the water quality of station, the government gave out a master plan until 2020 for using 100% surface water source [16]. However, assessing to the piped-water is still limited, for example in 2004, just less than 10% of people in the rural areas can utilize this water source, and the rest of them have to consume untreated water sources like ground water, surface water and rainwater for their daily living [17]. The survey of Wilbers for rural areas in Can Tho, Hau Giang and Soc Trang Province indicated that the percent of interviewed households using surface water, ground water, piped-water and rainwater for domestic services were 49%, 45%, 29% and 9%, respectively [18]. From that, it can be concluded that people living in the MD area mainly rely on surface water for their life due to its easy accessibility and free of charge source.

1.1.4 Some threats towards surface water resource

Although surface water is easily accessible and a cheap water source, its quality and quantity is facing up to many environmental problems, such as flooding, drought periods and climate change relevant to less rainfall and salinity intrusion. Besides that, the pollution coming from human wastes and the wastes from fish, poultry farming or pesticide is also dangerous threats.

1.1.4.1 Climate change

Climate change is one of the biggest challenges for mankind in the 21st century, affecting seriously to the production, life and the environment throughout the world. Temperature increases, sea level rises cause flooding, salt water intrusion and detrimental effects on agriculture. All of them creates a substantial risk for the industrial and socio-economic system in the future [11]. According to the report of the World Bank, Vietnam is one of the developing countries that are under the most severe influence of climate change, particularly at the coastal zones and the areas prone to flooding and drought. The MD becomes a seriously affected region where the climate change impacts are likely to bring new challenges as well as to magnify already existing ones. It impacts both the livelihoods and food security through making threat against surface water quantity and quality [19].
Two main natural obstacles as results of climate change in the MD area are drought and saltwater intrusion in dry season, affecting not only agriculture but also water supply and life for millions of coastal residents [11]. Annually, this phenomenon usually appears on the estuaries from about December of last year to May of following year with culminating around late April and early May. According to the mean lower low waters ($Z_{\text{min}}$: the average of all the lower low water heights of each tidal day observed over a specific 19-year Metonic cycle) in Figure 1-3, the average water level in the Tien and Hau rivers tend to decrease from 1985 to 2015. In the dry season 2016, the water level at Tan Chau station was extraordinarily low and lower long-term mean water level 0.9 m [20]. Some sections of the Mekong River flowing through Thailand have dried up so that ships could not circulate and the waterway transport was very difficult.

On the other hand, saltwater intrusion is also severe. In 2014, on the Tien River, the saltwater intrusion passed My Tho city of about 2-3 km, near the mouth of the channel Nguyen Tan Thanh, 57 km from the sea. On Hau River, the salinity came to channel head Number One (Soc Trang), 50 km from the sea. By comparing to salinity 4 g/l, saltwater could deepen 5-10 km, depending on different rivers. In 2016, saltwater intrusion has appeared two months earlier and has spread more widely and deeply into the system of major rivers in the western area, including the Tien River, Hau River, Vam Co River and Cai Lon River. In some areas, saltwater has intruded upstream 70-90 km into the mainland, that means 20-30 km deeper than previous years, and salinity rates are measured at 8-9‰ at some main river estuaries [21]. The results of several studies about the saltwater intrusion into estuaries of the MD area from 1980 to now pointed out that this phenomenon depends closely on 6 factors:
(1) The flow from the upstream Mekong river;
(2) The water storage capacity at end of flood season of the MD;
(3) Developments of coastal tide;
(4) Status of water used in the MD;
(5) The shape of river estuary;
and (6) The evolution of the monsoon season rainfall [22].
Figure 1-3: Mean lower low waters ($Z_{\text{min}}$) at Tan Chau Station and Chau Doc Station from 1985 to 2015

The intense drought and saline water created a great influence on the lives and production of residents (Figure 1-4). At many places, people lacked fresh water or had to buy it with very high price, 60000 VND/m³ (ca. 2.4 EUR/m³ in 2016), or even use the salinized piped-water with price of 10000 VND/m³ (ca. 0.4 EUR/m³ in 2016). Nearly 40% of the MD’s acreage suffered from excessive salinity, which damaged around 200,000 ha of winter-spring rice and vegetable crops. In Ben Tre Province, nearly all of the "Coconut Island" sank in salt water [23]. According to the Irrigation Departments of Hau Giang Province, almost 6,000 ha of production land at Luong Tam, Luong Nghia, Xa Phien, Vinh towns was affected by saltwater with 5 - 6‰. Furthermore, hundreds of fruit trees and aquaculture areas were also impacted by the lack of fresh water [24].
Chapter 1  |  Literature review

Figure 1-4: Effects of drought and saltwater intrusion production on residents: a) Paddy field was damaged; b) The saltwater intrudes the paddy field; c) Fruit orchards were sunburned due to freshwater shortage; d) Mortality of shrimps in dried aquaculture field [23], [24].

1.1.4.2 Flooding

Besides drought and saltwater intrusion, flooding is also a consequence of erratic climate change in the MD. According to the newest analysis (January 2016) on the impact of flooding on Gross domestic product (GDP) of the World Resources Institute (WRI), in the 164 countries surveyed, Vietnam was ranked 4th in terms of harm of flooding to the entire economy as 80% of the population is affected. The organization also has reported that flooding is costing 2.3% of Vietnam's GDP each year, and if sea level rises by 1 meter, an estimated 40% of the area of the MD will be submerged [25].

The annual seasonal flooding is an unavoidable problem due to the low elevation of the MD. Areas that can keep flood represent just over 3% of the basin while the flow of flood season is very high, like for instance up to 65,000 m³/s in 1939. In the flood season, the flow of Mekong
River increases rapidly with peaks from late September to mid-October, causing flooding in large parts of the delta. Flooding on the whole area of the delta is up to 3-4 million ha, and flood lasts 2-5 months with flood depths from 0.5 m to more than 4 m (Figure 1-5) [11].

Flooding spreads at many large parts of the MD’s provinces and seriously affects the lives, production situation of the people as well as water resource quality. The Central Committee for Flood and Storm of the MD indicated that in years of large floods like 1994, 2000, 2002, there were thousands of houses flooded deep and collapsed which could not guarantee the safety of residents. Many schools were closed because of floodwaters, so that students had to stop their studies for a long time. The production of people was damaged remarkably because farmland has been washed away and riparian land was heavy landslides. Many households suffered from food shortages, freshwater scarcity [10]. Since the floodwater spreads dirt, domestic waste and livestock from residential areas out to water sources, causing surface water pollution. This happened at many provinces, because sewage, municipal waste and livestock from households were not managed properly.

In conclusion, dangerous impacts of climate change and sea level rise in the MD is mainly risk of freshwater shortage, affecting very negatively all aspects of life, society and economy.

1.1.4.3 Impacts of human activity on surface water source

In addition, human activities are also one of the major threats to water quality. The urbanization rate is increasing quickly, but the development of infrastructure for water supply is asynchronous which leads to discharge of the waste water directly into the environment, affecting hazardously to surface water quality [27]. For example, in the MD, covering of acid sulfate soils
(ASS) on nearly 40% of the total agricultural surface area increases the mobility of toxic elements, potentially influencing crop production, aquatic organisms and drinking water sources [12]. The concentrations of heavy metals in surface water especially Al ( > 100 mg/L) exceeds the toxicity levels for fish and plant roots [28].

Moreover, the agricultural activities as well as aquaculture are also considered as the main source of pollution. Shrimp and fish farming decrease levels of (bio) chemical oxygen demand (COD, BOD), nutrients in water, and concentrations of dissolved oxygen (DO) [12]. The uncontrollable and unscientific overuse of fertilizer and pesticide induces an increase of their residues in the environment. Particularly, the amount of imported pesticides rose quickly from 1990 to 2004 [29], and farmers in the MD used them significantly more than in the Red River Delta (applied 5.3 times per crop season) [30]. The lack of awareness of the people when using these fertilizers or pesticides is a dangerous threat toward water source quality, such as discharging empty pesticide containers directly in the fields, pouring the left-over pesticide solutions directly in fields or into canals, cleaning the sprayers in irrigation ditches or ponds within their fields, or washing the equipment in canals outside the field.

1.1.5 Surface water quality

Due to the disasters and the human activities, the surface water source in the MD is seriously influenced on quantity and quality. Many water quality studies have been carried out in the MD. [[1]–[3], [12], [31]–[33]]. Surveying and evaluating water quality have been conducted continuously by an annual monitoring program of Ministry of National Resource and Environment (MONRE) of Viet Nam. In this program, samples are taken four times per year covering both the dry season and the rain season, at thirty five points in the two main waterways (Tien River and Hau River) from the upstream to downstream (Figure 1-6). Monitoring parameters include physical-chemical parameters, nutrition components, salts, metals, microbial indicators and organic pollutants, such as pesticides. Results of parameters are compared with the National technical regulation on drinking water quality enacted by the Ministry of Health (MOH), QCVN 01:2008/BYT [34]. The parameters which are not mentioned in QCVN 01:2008/BYT are compared with the National technical regulation on surface water quality enacted by the MONRE, QCVN 08:2009/BTNMT – class A2 [35] (class A2 is quality of surface water used for domestic water supply). The monitoring results carried out in 2012 of some basic parameters are indicated in Table 1-1. The analysis and assessment about the pollution level of parameters are summarized in the following sections.
Figure 1-6: Map of sampling points in Tien River and Hau River [36]
### Table 1-1: Results of the environmental monitoring in Mekong Delta from 3/2012 - 11/2012 [36]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>VN guideline</th>
<th>Inland region</th>
<th>salinity intrusion region</th>
<th>N</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
<th>N</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
<th>N</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
<th>%drink&lt;sup&gt;a&lt;/sup&gt;</th>
<th>N</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
<th>%drink&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC (dS/m)</td>
<td>–</td>
<td>46 0.126 0.237 0.2</td>
<td>46 0.106 0.156 0.2</td>
<td>46 0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.5–8.5</td>
<td>46 6.3 8.3 7.2</td>
<td>46 6.3 7.7 7.2</td>
<td>46 6.6 7.9 7.4</td>
<td>26 7.2 8 7.4</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>30&lt;sup&gt;b&lt;/sup&gt;</td>
<td>46 36 100 60.3</td>
<td>46 11 229 108.8</td>
<td>95 26 46 157 96.7</td>
<td>26 32 232 93.5 100</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>&gt;=5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>46 2.8 7.5 5.4</td>
<td>46 4.5 7.6 5.4</td>
<td>13 26 4.8 7.6 6.1</td>
<td>26 5 7.5 6.1 0</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>46 2.85 10.92 5.5</td>
<td>46 2.92 11.23 5.5</td>
<td>0 26 3.45 13.4 7.1</td>
<td>26 3.85 17.44 7.1 1.9</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl (mg/L)</td>
<td>250</td>
<td>46 12.8 51.8 20.6</td>
<td>46 5.57 40.19 20.6</td>
<td>0 26 29 13887 3184</td>
<td>26 7 3338 231.6 42</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO4 (mg/L)</td>
<td>250</td>
<td>46 4.32 26.16 10.7</td>
<td>46 1.87 7.87 10.7</td>
<td>0 26 16.22 1763 449.1</td>
<td>26 3.46 502 48.8 25</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nutrients</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH4 (mg/L)</td>
<td>3</td>
<td>46 0.02 0.18 0.1</td>
<td>46 0.02 0.32 0.1</td>
<td>0 26 0.01 0.24 0.1</td>
<td>26 0.02 0.13 0.1 0</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3 (mg/L)</td>
<td>50</td>
<td>46 0.03 0.68 0.3</td>
<td>46 0.08 0.43 0.3</td>
<td>0 26 0.15 0.61 0.4</td>
<td>26 0.17 1.12 0.4 0</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-PO4 (mg/L)</td>
<td>0.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>46 0.011 0.104 0.1</td>
<td>46 0.026 0.205 0.1</td>
<td>1 26 0.022 0.159 0.1</td>
<td>26 0.028 0.181 0.1 0</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microbial indicators</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. coli (CFU/100mL)</td>
<td>0</td>
<td>46 4 9300 574</td>
<td>46 4 900 574</td>
<td>100 26 15 1500 279</td>
<td>26 4 400 279 100</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coliform (CFU/100mL)</td>
<td>0</td>
<td>46 90 43000 4549</td>
<td>46 900 1E+05 4549</td>
<td>100 26 230 1E+05 9767</td>
<td>26 430 46000 9767 100</td>
<td>0</td>
<td>0.003 35.54 4.7</td>
<td>26 0.122 11.92 4.7</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N: Number of samples

<sup>a</sup> QCVN 01:2008/BYT

<sup>b</sup> QCVN 08:2009/BTNMT – class A2

<sup>c</sup> Percentage of water samples exceeding the Vietnamese guidelines
1.1.5.1 Salts

Salt concentrations in surface water in the MD are mainly dependent on weather conditions as shown in Table 1-1. During the dry season from December to May, the reduced amount of rain combined with the reduced amount of water upstream leads to salinization (as described above), causing the rise of salt concentrations in surface water, especially at downstream areas. In contrast, during the rainy season from June to November, concentrations of these indicators do not exceed the permitted standard (Viet Nam Guidelines).

According to the environmental monitoring report in the MD in 2012 [36], the concentration of Cl\(^{-}\) at upstream regions (areas not affected by saltwater) almost achieved national technical regulation for drinking water quality (Cl\(^{-}\) = 250 mg/l). However, in the coastal regions, concentration of Cl\(^{-}\) was very high with 42% of samples in excess of the guideline and the maximum value was 13887 mg/l. This trend was similar to the study of Wilbers et al. [12] in the secondary canals. It was observed that concentration of Cl\(^{-}\) at coastal areas exceeded Viet Nam Guidelines for almost all samples. The highest value was 18070 mg/L and surface water in these areas could not be used for drinking water and domestic purposes, even irrigation for agriculture. Similarly, concentration of \(\text{SO}_4^{2-}\) at upstream regions was lower than 20 mg/L which is 10 times lower than water quality standards (250 mg/L). On the contrary, the seawater intrusion affecting coastal areas in the dry season induced the high values of sulfate ions (\(\text{SO}_4^{2-}\) > 600 mg/l).

Regarding the concentration of Cl\(^{-}\) in water, it is possible to divide the MD into two regions: (i) inland region where the concentration of Cl\(^{-}\) in water over one year does not exceed the threshold of drinking water quality (250 mg/L); and (ii) salinity intrusion region has concentrations of Cl\(^{-}\) exceeding this threshold. From this it can be shown that sea water intrusion could reach 30 – 40 km inland along rivers during the dry season of 2012. Saltwater intrusion has seriously affected the quality of surface water in the area. Hence, it is necessary to have a consistent treatment process for desalination before providing water for domestic as well as drinking needs of the people.

1.1.5.2 Physical-chemical parameters

In general, the parameters concerning the physical and chemical characteristic of the MD surface water reported in Table 1-1 were within the permitted limits of the quality of drinking
water or surface water quality for domestic purposes according to the environmental monitoring report in the MD in 2012 [36]. Particularly, it is as follows:

The electrical conductivity ($\sigma$) of the water reflects the total amount of dissolved solids in solution (TDS), and for surface water, this parameter is determined by the concentration of salts in the water. In the MD, the change of conductivity in surface water follows the variation of Cl$^-$ concentration. In 2012, the conductivity of surface water in the inland region was much lower than in the salinity intrusion region, and in the dry season was usually higher than during the rainy season (Table 1-1). These observations were attributed to seawater intrusion and droughts.

Values of pH reflect levels of H$^+$ ions in water. The pH value at the monitoring points ranged from 6.3 to 8.3. There was no significant difference in average pH value of the samples between different seasons and in various regions, 7.2 and 7.4 in the inland and salinity intrusion regions, respectively. However, 16% of the sample in inland areas was somewhat lower than the lower limit of the QCVN for drinking water.

Dissolved oxygen (DO), the amount of oxygen that is present in the water, and chemical oxygen demand (COD) reveal levels of pollution caused by the organic matters. Results of DO and COD in monitoring samples on the Tien River and Hau River were quite good, most of them attaining the technical requirements for surface water. The number of samples exceeding the DO standard in the inland region is higher than that in the salinity intrusion region, 13% and 3.8%, respectively. It was observed that DO concentration of the samples in the inland region was lower than that in the salinity intrusion region. A similar finding was reported in the study of Wilbers et al. [12], and the reason was attributed to seawater intrusion, which is normally less polluted than river water.

Different from other parameters, the percentage of samples which their total suspended solids (TSS) exceeded the surface water standard for domestic water (30 mg/L) was very high, with 95% of the samples in inland areas and all of samples for salinity areas. The cause of this phenomenon came from the characteristics of the surface water at South West containing a lot of silt. Although TSS value exceeded the class A2, the TSS value did not have much impact on aquatic life. On the other hand, the silt source was very useful for irrigation water use and accretion of land resources. However, if used for domestic and drinking water, it is necessary to remove this silt.
1.1.5.3 Nutrients

The concentration in river water of nitrogenous nutrients, including ammonium (NH$_4^+$), nitrite (NO$_2^-$) and nitrate (NO$_3^-$) mainly comes from the run-off of land surface and the production activities in the region, such as fertilizers from farming, wastewaters from processing of frozen seafood exports, aquaculture sectors or domestic uses of people. The monitoring results in Table 1-1 showed that the concentration of nitrogenous components in surface water was very low and several times lower than the surface water guidelines. The maximum values in the inland and the salinity areas respectively were 0.32, 0.24 for NH$_4^+$ and 0.68, 1.12 for NO$_3^-$. In contrast to these results, Wilbers’s study [12] showed that the concentration of nitrogenous components was higher in the secondary canals likely because these channels directly receive wastewater from the fields where were applied a large amount of fertilizers and from domestic wastewater of the people. Also as a result, concentration of PO$_4$ in most samples in both inland and salinity regions was below the surface water guidelines.

In brief, nutrient concentrations in surface water were within permissible limits and did not depend on weather conditions as well as geography.

1.1.5.4 Microbial indicator bacteria

Microbial indicators used to assess the quality of the water environment are Coliform and E. coli. These parameters relate directly to water resources affected by domestic sewage (feces) or by the decomposition of animal residues (in the seafood processing). The reinfection ability or contamination development of Coliforms in rivers is complex and depends mainly on the pollution composition and sources.

These parameters directly affect the human health, and often cause intestinal diseases like diarrhea. Therefore, the standard for drinking water quality does not permit the presence of these microbial indicators. However, all of surface water samples in the MD were contaminated as these indicators in Table 1-1 exhibit values from 4-9300 CFU/100mL for E. coli and 90-110000 CFU/100mL for Coliform. The values in the dry season tended to be higher than in other periods of the year. These microbial indicators thus must be treated before a water supply can be used for domestic and drinking water.

Although microbial indicators are widely detected in the MD, households usually treat surface water (e.g. boiling and/or chemically) prior to drinking which could decrease the actual health risks associated with consuming surface water.
1.1.5.5 Metals

The occurrence of heavy metals in surface water is due to mining, or human activities (such as production activities), exploitation of natural resources, agriculture cultivation, etc. In water, heavy metals can exist in various forms, such as adsorbed on the surface of suspended solids, linked in organic solids or dissolved in solution under structures of ions or complexes. Heavy metals existing under soluble form have the lowest concentration in natural surface water sources. Similarly, water sources from Tien River and Hau River contain only small concentrations of soluble heavy metals (Table 1-2).

Table 1-2: The concentration of heavy metals in Mekong Delta from 3/2012 - 11/2012 [36]

<table>
<thead>
<tr>
<th>Metals</th>
<th>VN guideline</th>
<th>Detection Frequency (%)</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (mg/L)</td>
<td>0.01</td>
<td>53.1</td>
<td>0.003</td>
<td>0.012</td>
<td>0.005</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.003</td>
<td>31.3</td>
<td>0.0006</td>
<td>0.0009</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.3</td>
<td>100</td>
<td>0.21</td>
<td>1.88</td>
<td>0.983</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>1</td>
<td>91.7</td>
<td>0.002</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0.01</td>
<td>0</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Cr^{6+} (mg/L)</td>
<td>0.05</td>
<td>0</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>0.02</td>
<td>8.3</td>
<td>0.0007</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Hg (mg/L)</td>
<td>0.001</td>
<td>0</td>
<td>&lt; 0.0002</td>
<td>&lt; 0.0002</td>
<td>&lt; 0.0002</td>
</tr>
</tbody>
</table>

Monitoring results of heavy metal concentrations, such as As, Cd, Fe, Cu, Pb, Cr, Ni, and Hg in river water showed that they were virtually undetectable or lower than drinking water guidelines, exception for iron [36]. Concentration of iron (Fe) in samples was from 0.2 – 1.8 mg/L and the majority of the samples exceeded the surface water guidelines. Heavy metal concentrations in secondary canals, according to the report of Wilbers et al. [12], are higher than in the river water, especially in coastal regions. The heavy metals exceeding drinking water guidelines included As, Cr, Hg, Mn, Al, Fe. The presence of these metals in secondary canals makes the consumption of this water kind of dangerous. However, according to the monitoring results in main rivers [36], as well as report of Mekong River Commission 2007 [37], the presence of metals in the river was not harmful to human health.
1.1.5.6 Pesticides

The development of agricultural production, mainly rice production, has led to a rapid increase in pesticide use. Before 1992, there were only 77 active ingredients with 96 product names that were used. By 2008, there were more than 700 active ingredients with more than 2,800 product names. Imported pesticide quantities rose to nearly 50,000 tons/year in 2004 from 13,000 – 14,000 tons/year before 1990. [29], [38], [39]. Although it is recognized the tremendous benefits of pesticide utilization, unscientific and uncontrollable handling and applying of pesticides have induced a strong rising their occurrence in surface water [39].

In the recent studies [40]–[42] and also in the monitoring environment report [36], it was reported that the residues of persistent organochlorine and organophosphate pesticides have not been detected in surface water in the MD since their use was banned in 1989. However, the residues of recently used pesticides were detected in many places in the MD. In the study of Carvalho *et al.* [41], diazinon, and fenotrothion were detected in canal water samples near rice field with concentration ranging from 0.003 to 0.043 µg/L. In river water, the concentration of residues was lower.

In 2008, the pesticide usage of farmers was surveyed by interviewing households and the occurrence of commonly used pesticides in the irrigation canals was determined and accessed in two provinces Can Tho and Dong Thap by Toan *et al.* [2]. The study revealed the co-occurrence of a wide pesticide range in many samples throughout the year with considerable concentration. For instance, isoprothiolane was the most frequently detected pesticide (in 100% of the samples) with concentrations ranging from 0.02 to 11.24 µg/L followed by fenobucarb (in 90.8% of samples) with concentration ranging from 0.02 to 1.43 µg/L. These pesticide residues in many samples exceeded the guideline for drinking water set by the Drinking Water Directive (98/83/EC). The other pesticides with a high quantification frequency comprised pretiachlor (68.9%), buprofezin (58.7%), fipronil (48.5%) and propiconazonle (45.9%). These pesticides were also detected in canal waters in An Giang Province and some other districts in Can Tho Province by Chau *et al.* [1] with high frequency. The median concentration of isoprothiolane was 0.55 µg/L while that of fipronil and fenobucarb was 0.17 and 0.15 µg/L, respectively. Over 80% of samples contained more than five pesticides simultaneously and 95% of samples exceeded the EC guideline value for concentration of total pesticides in drinking water (0.5 µg/L). Especially, this study indicated that the pesticide residues in surface water at three pump stations located in the Hau River, Sang Trang Canal, Thom Rom Canal where extracted surface water for water
supply stations in Can Tho City, again exceeded the EC guideline value in almost all the of analysed samples.

Shortly, although the residues of persistent pesticides are no longer detected in surface water in the MD, the co-occurrence of recently used pesticides was detected frequently and exceeded the guideline concentrations in the entire delta. It is thus concluded that pesticide pollution in the MD is ubiquitous. Especially, the most polluted sources are canal waters, which are the main source for drinking water and other domestic purposes.

1.1.5.7 Target of treatment

In conclusion, the amount of surface water in the MD is very great and transported through many kinds of canals and different rivers. Each type has its own function, as well as various flow rates. Therefore, the pollution composition and pollution level in each kind were also different, as presented above. Some pollution components exceeded the permissible standards of drinking water, such as salinity, TSS, microbial bacteria, heavy metals and pesticide residues. This study is focused on salinity and pesticide residues and aims at treating them by using membrane technology to respect the drinking water guidelines. Other parameters can be removed by water using people habits (filtering and boiling), such as TSS and microbial bacteria, or removed simultaneously with the process of desalination.

For logistic reasons, this study was limited to the laboratory scale with synthetic model water samples representative of surface water found in the MD. As for the salinity component, based on salt data in the Table 1-1, it can be seen as follows: in the salinity intrusion region, the maximum value and the median value of chloride ion concentration during the dry season were 13887 mg L\(^{-1}\) and 3184 mg L\(^{-1}\), respectively and those of the sulfate ion were 1763 mg L\(^{-1}\) and 449 mg L\(^{-1}\), respectively. The maximum value in the rainy season was quite similar to the median one in the dry season. The median and the minimum values in the rainy season were lower than those of Vietnamese drinking water guideline. Thus, the synthetic model water samples were prepared with two levels of salts which were the maximum and the median values of the samples during dry season. They were representative of river water in the salinity intrusion region.

Regarding the pesticide composition, based on the research results of Toan et al. [2] and Chau et al. [1], three kinds of specific pesticides (insecticide, fungicide and herbicide) were detected most frequently which will be selected for this study. They are fenobucarb, isoprothiolane and pretilachlor. These pesticides also have physical properties representative of
the other pesticides, as for example their molecular weight varying from the lowest of fenobucarb (207.3 g mol\(^{-1}\)) to the highest of pretilachlor (311.8 g mol\(^{-1}\)).

1.2 Nanofiltration

1.2.1 Introduction

The term “nanofiltration” was introduced by FilmTec in the second half of the 1980s to describe a “reverse osmosis process” that selectively and purposely allows some ionic solutes in a feed water to permeate through certain types of membranes [43]. Nanofiltration (NF) membranes were developed from older membranes like ultrafiltration (UF) and reverse osmosis (RO) ones. Therefore, it was defined as “an intermediate process between RO and UF that rejects molecules which have a size in the range of one nanometer”. The “loose RO” property (larger membrane pore structure) of NF membranes enables them to be operated at higher water fluxes with much lower pressure compared to RO membranes, which results in significant energy saving [44]. While the “tight UF” property helps them to eliminate multivalent salts near completely and remove relatively small organic compounds.

The NF membranes operate with sieving mechanisms owing to their porous structure. In addition, most NF membranes have charged surfaces so that electric interactions also affect their transport and selective rejection behavior. Some properties of NF in comparison with RO and UF are shown in Table 1-3.
Table 1-3: Comparison of properties between NF, RO and UF [4]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ultrafiltration</th>
<th>Nanofiltration</th>
<th>Reverse osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membranes</td>
<td>Asymmetric porous</td>
<td>Composite</td>
<td>Asymmetric or composite</td>
</tr>
<tr>
<td>Thickness</td>
<td>≈ 150 µm (or monolithic for some ceramics)</td>
<td>sublayer ≈ 150 µm toplayer ≈ 1 µm</td>
<td>sublayer ≈ 150 µm toplayer ≈ 1 µm</td>
</tr>
<tr>
<td>Pore size</td>
<td>≈ 1-100 nm</td>
<td>&lt; 2 nm</td>
<td>&lt; 0.5 nm (non-porous)</td>
</tr>
<tr>
<td>Driving force (Pressure)</td>
<td>1 – 10 bar</td>
<td>3 – 20 bar</td>
<td>brackish water 15-25 bar seawater 40-80 bar</td>
</tr>
<tr>
<td>Separation principle</td>
<td>sieving mechanism</td>
<td>Sieving and Donnan exclusion</td>
<td>solution-diffusion</td>
</tr>
<tr>
<td>Membrane material</td>
<td>polymer (polysulfone, polyacrylonitrile) ceramic (zirconium oxide, aluminium oxide)</td>
<td>polyamide</td>
<td>cellulose triacetate, aromatic polyamide, polyamide and poly(ether urea)</td>
</tr>
<tr>
<td>Rejection for monovalent ions</td>
<td>0%</td>
<td>10 - 90%</td>
<td>&gt; 98%</td>
</tr>
<tr>
<td>Rejection for bivalent ions</td>
<td>0%</td>
<td>70 - 99%</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>Bacteria and viruses</td>
<td>&lt; 99%</td>
<td>&lt; 99%</td>
<td>&gt; 99%</td>
</tr>
<tr>
<td>Macro-solutes (Mw &gt; 100)</td>
<td>0%</td>
<td>&gt; 50%</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Micro-solutes (Mw &lt; 100)</td>
<td>0%</td>
<td>0 – 50%</td>
<td>0 – 99%</td>
</tr>
</tbody>
</table>

In recent years, NF has emerged in water treatment as an optimal method with many advantages. Firstly, the lower working pressures as well as the higher fluxes lead to lower operation costs. Secondly, it is particularly effective in the removal of organic molecules with molecular weights in range of 200 – 1000 Da. In addition, the high exclusion of bivalent ions and
the low exclusion of monovalent ions lead to the high selectivity in applications targeting the separation of ions [45].

However, there are still some disadvantages of NF membranes. The most important drawback is the difficulty in controlling the reproducibility of the membrane pore size and the pore size distribution [43]. Besides, membrane fouling is also a problem, inducing the flux decline in applications [46].

1.2.2 Application

NF membranes have found their applications in many fields, such as the food industry, chemical processing industry, wastewater treatment or water reuse, and drinking water production. In the food industry, NF is efficiently applied in processes of concentration and demineralization of whey, or concentration of dextrose syrup and thin juice [47]. The highlights in the chemical processing industry are applications in pharmaceutical production and biotechnology, or in purification and concentration chemical processes. Some important applications in wastewater treatment concern the removal of heavy metals from wastewater [48], the regeneration of brewery wastewater [49], and the decolorization of textile wastewater [50].

NF started to be used for drinking water production in the late 1980s for treatment of hard and colored water in Florida. Today, it is still applied in water softening and removing other dissolved components: nitrate, sulfate, fluoride and heavy metals. Its capacity in removing dissolved organic components and organic pollutants has been studied in the laboratory and also applied in large scale plants for over 15 years. A successful example is the Mery-sur-Oise plant installed in France, which uses NF technology to produce drinking water from the river Oise [51].

Application of NF in desalination is considered in many studies in order to take full advantage of the low energy consumption. However, NF is currently efficiently applied only in the pretreatment step due to its low monovalent ion rejection. NF is then usually combined with other membrane processes, such as RO and multistage flash (MSF). The benefits of using NF as pretreatment include preventing RO membrane fouling and scaling by the removal of turbidity, bacteria, and lowering the required operating pressure by reducing the seawater feed TDS [43].
1.2.3 Transport through the membrane

1.2.3.1 Exclusion mechanisms

The removal of solutes by NF membranes is performed by two main exclusion mechanisms, size exclusion and Donnan exclusion. Size exclusion or sieving is based on the relation between the pore size of membrane and the size of permeating particles. The pore size of NF membranes is typically around 1 nm, so their molecular weight cut off (MWCO) is in the range of 200 – 300 Da. It means that the compounds that have higher molecular weight than the MWCO will be rejected and lower ones will be transferred. It was proved that the larger the solutes, the greater the size effect and pollutant retention [44]. However, this mechanism gives only a rough estimate of the retention characteristics of a membrane for uncharged compounds.

Furthermore, the pores of NF membranes also have a surface charge. Polymeric NF membranes contain ionizable groups, e.g., carboxylic or sulfonic acid groups, which result in a surface charge in the presence of a feed solution. The equilibrium between the charged membrane and the bulk solution is characterized by an electric potential, the Donnan potential, which retains ionic species. This mechanism (so-called Donnan exclusion) allows the removal of ions with a size below the pore size of the membrane [52]. However, the relative contributions of these two basic mechanisms involved in the NF process differ from case to case, and cannot be simply assessed because all the operating mechanisms have not been completely understood yet [53].

1.2.3.2 Modeling models of transport

Modeling is a considerable research subject in membrane technology with the goal of predicting the performance of a system. Modeling in NF technology includes two main aspects: flux prediction and rejection prediction. These aspects not only bring a full understanding of a lab-scale membrane module but also can enable the scale up to larger installations. A good predictive model will allow users to obtain membrane characteristics as well as to optimize the process. Depending on membrane characteristics and solute properties, different models have already been proposed such as the pore model and the hindered electro transport (HET) model described by the extended Nernst – Planck equation and modified to included hindered transport [54].

1.2.3.2.1 Pore model

The pore model assumes that there is the presence of open micropores on the top layer of the membrane through which the mass transport occurs and all the micropores have the same
radius. Interaction parameters are not considered and viscosity is the only solvent parameter. The volume flux through these pores can be described by the Hagen–Poiseuille equation as follows [55]:

\[ J_v = \frac{\pi r^2 \Delta P}{8 \mu r \Delta x} \]  

(1-1)

where \( J_v \) is the flux of solvent (L.h\(^{-1}\).m\(^{-2}\)), \( r \) is the pore radius (m), \( \varepsilon \) is the surface porosity, \( \varepsilon = n_p \pi r^2 / A_m \) (\( A_m \) is the membrane area, \( n_p \) is the number of pores), \( \mu \) is the fluid viscosity (Pa s), \( \tau \) is the pore tortuosity, \( \Delta P \) is the pressure difference (bar) and \( \Delta x \) is the thickness of the membrane (m). This equation clearly shows the effect of membrane structure on transport and indicates that the solvent flux is proportional to the pressure difference as the driving force.

For membranes consisting of spherical particles, which can be found in organic and inorganic sintered membranes or in phase inversion membranes with a nodular top layer structure, Kozeny-Carman’s law can be used [56]:

\[ J_v = \frac{\varepsilon^3 \Delta P}{K \mu S^2 (1-\varepsilon)^2 \Delta x} \]  

(1-2)

where \( \varepsilon \) is the porosity; \( S \) is the internal surface area, \( K \) is the Kozeny-Carman constant, which is dependent on the pore shape and tortuosity.

The pore model is just an approximate model where the porous membranes are represented as a bundle of straight cylindrical pores and solute transport is corrected for hindered convection and diffusion. This model may not suffice for describing an extremely complex system (solute and NF membrane) where not only hindered and diffusive interactions, but also electrical interactions as well as irreversible thermodynamics, affect the transport.

1.2.3.2.2 Hindered electro transport (HET) model

The hindered electro transport (HET) model is generally used to describe the salt transport through NF membrane, in which both the electrostatic and hindered transport effects are taken into account [54]. The transport of neutral solute can also be modeled by not considering the electrostatic interactions. This model is based on the volume averaged Stokes equation for solution flow and incorporates steric and hydrodynamic hindrance factors into the Extended Nernst–Planck (ENP) solute flux equations and steric/Donnan partitioning at the membrane-solution interfaces. The volume averaged Stokes equation for the flux of a permeate solution takes the form:
where \( J_v \) is the flux of permeate solution or the volume flux density (L.h\(^{-1}\).m\(^{-2}\)), \( L_p^0 \) is the pure water permeability coefficient (L.h\(^{-1}\).m\(^{-2}\).bar\(^{-1}\)), \( p \) is the pressure (bar), subscripts \( i \) and \( m \) denote the \( i \)th component and membrane, respectively, \( c_{im} \) (mol/m\(^3\)) and \( \gamma_{im} \) are the concentration and the effective activity coefficient of \( i \) in the membrane, \( \rho(x) = F \sum_i z_i c_{im}(x) \) is the local ion charge density, \( \varphi \) is electric potential in membrane (V), \( R \) is the gas constant and \( T \) is the absolute temperature.

Integrating equation (1-3) over the membrane thickness yields \( 0 < \Delta x \) and assuming that the gradient of \( \ln \gamma_{im} \) can be neglected because the concentrations of solutes in membrane are small or their variations are small, we obtained:

\[
J_v = -L_p(\Delta P_e) \tag{1-4}
\]

where \( L_p \) is the effective permeability including the effects of electro-viscosity, given by:

\[
L_p = \frac{L_p^0}{(1+\kappa)\Delta x} \tag{1-5}
\]

with \( \kappa \) the electro-viscosity coefficient. In the good co-ion exclusion (GCE) approximation for the HET model, it takes the following simple form [57]:

\[
k = \frac{RTL_p^0 \xi_m |X_m| K_{1,c} \ell_{eff}}{|\varepsilon_1| K_{1,d} D_1 \Delta x} \tag{1-6}
\]

where subscript \( 1 \) denote to the counter ion, \( X_m \) is the effective membrane charge density (moles per unit pore volume – mol/l), \( K_{1,c} \) and \( K_{1,d} \) are the convective and diffusive hindrance factors, \( \ell_{eff} \) is the effective active NF membrane layer thickness (µm), \( D_1 \) is the counter ion diffusion coefficient in bulk solution (m\(^2\)/s). The GCE is valid at low feed salt concentration, \( C_f \), or high membrane charge density, i.e., when the \( X_m/C_f >> 1 \).

In equation (1-4), \( \Delta P_e \) is the effective pressure driving force (bar), which is the difference from the trans-membrane pressure (\( \Delta P \)) by the inclusion of the osmotic pressure difference across the membrane. The effective pressure is written as:

\[
\Delta P_e = \Delta P - \sigma \Delta \pi \tag{1-7}
\]
where $\Delta\pi$ is the osmosis pressure (bar) and $\sigma$ is the osmotic reflection coefficient, a parameter that measures the degree of semi-permeability of the membrane reflecting its ability to pass solvent in preference to solute.

Substituting equation (1-7) into equation (1-4) we can obtain:

$$J_v = -L_p(\Delta P - \sigma\Delta\pi)$$

(1-8)

The hindered ENP equations take into account the contributions not only of diffusive flow, electric migration flow and convective flow but also ion size and other interactions to the ion flux. This equation is [58]

$$J_i = -c_{im}D_{im} \frac{d[ln\gamma_{im}]}{dx} - D_{im} \frac{dc_{im}}{dx} - \frac{z_i c_{im} D_{im} F}{RT} \frac{d\varphi}{dx} + K_{ic} c_{im} J_v$$

(1-9)

where subscript $i$ and $m$ denote to ion and membrane, $D_{im}$ is the diffusion coefficient of $i$ in membrane ($m^2/s$), $z_i$ is the ion valency $i$, $F$ is the Faraday constant and $K_{ic}$ the hindrance factor for convection of ion $i$.

The equation (1-9) shows that the ion flux ($J_i$) depends on the volume flux density ($J_v$) crossing the membrane, and only indirectly on $\Delta P$ via $J_v$.

The ion flux can also be written as:

$$J_i = C_{pi} J_v$$

(1-10)

where $C_{pi}$ is ion bulk permeate concentration (mol/m$^3$).

Assuming the gradients of $ln\gamma_{im}$ can be neglected, substituting equation (1-10) into equation (1-9), collecting terms in $c_{im}$ and rearranging results in the following expression for the concentration gradient:

$$\frac{dc_{im}}{dx} = \frac{J_v}{D_{im}} \left[K_{ic} c_{im} - C_{p} \right] - \frac{z_i c_{im} D_{im} F}{RT} \frac{d\varphi}{dx}$$

(1-11)

Spatial averaging of Poisson equation leads to the approximate electroneutrality condition in the membrane,

$$\sum_{i=1}^{n} z_i c_{im} + X_m \approx 0$$

(1-12)

The electric potential gradient can be taken by the summation over all ions:

$$\frac{d\varphi}{dx} = \frac{\sum_{i=1}^{n} z_i c_{im}}{F \sum_{i=1}^{n} z_i^2 c_{im}} \left[K_{ic} c_{im} - C_{p} \right]$$

(1-13)
The calculation procedure based on the integration of equations (1-11) and (1-13) with the condition (1-12) allows one to model the relation of rejection \( R = 1 - \frac{c_p}{c_f} \) as a function of volume flux \( \dot{V}_f \). If steric exclusion is for the moment neglected, the limiting transmission coefficient takes on a simple form within the GCE approximation:

\[
T = \frac{c_p}{c_f} = \frac{k_f}{t_1} = \left( 1 + \frac{|z_2|D_{2,m}}{|z_1|D_{1,m}} \right) \left( \frac{\xi}{v_1|z_1|} \right)^{|z_2|/|z_1|} \tag{1-14}
\]

and the limiting rejection

\[
R = 1 - T = 1 - \frac{k_f}{t_1} \tag{1-15}
\]

where \( T \) is the limiting transmission coefficient, subscripts 1 and 2 denote the counter ion and co-ion, \( z \) and \( v \) are electrochemical valence and stoichiometric coefficient of ion, \( t_1 \) is transport number of counter ion (dimensionless), \( k_f \) is the Donnan co-ion partition coefficient at the feed-membrane interface in the GCE approximation (dimensionless) and given by:

\[
k_f = \left( \frac{\xi}{v_1|z_1|} \right)^{|z_2|/|z_1|} \tag{1-16}
\]

where \( \xi \) is the normalized membrane charge density (dimensionless) and given by:

\[
\xi = \frac{x_m}{c_f} \tag{1-17}
\]

In the expression for \( T \) (equation (1-14)), the first term in parentheses comes from co-ion convection, the second term in parentheses comes from co-ion migration in the streaming field induced by the counter-ions, and the last multiplying factor comes from Donnan co-ion partitioning in the GCE approximation.

In the HET model, partition coefficients depend on electrostatic effects and steric hindrance effects and are given by [54]:

\[
k_i = \frac{c_{im}}{c_i} = \Phi_i exp \left( - \frac{z_iF}{RT} \Delta \varphi_D \right) \tag{1-18}
\]

where \( \Delta \varphi_D \) is the Donnan potential (V), \( \Phi_i \) is the steric hindrance partition coefficient of ion i, defined as \( \Phi_i = \left( 1 - \frac{r_i}{r_p} \right)^2 \), where \( r_i \) and \( r_p \) are the ion and the pore radii, respectively. It is usually assumed in the literature that the ion size obeys the Stokes-Einstein relation
where $r_i^S$ is the radius of the solute (m), $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J.K$^{-1}$), $T$ is the temperature (K), and $\eta$ is the dynamic viscosity (= $1.0019 \times 10^{-3}$ Pa.s 20°C).

Although the Stokes radius is justified in the case of neutral solutes, it is not true in the case of ions. For ions the bare ion crystal (or Pauling) radius is most likely a better choice and is thus used for calculations using the Nanoflux® software.

1.2.3.3 Nanoflux®

1.2.3.3.1 Introduction

It is known that in NF solute rejections depend on the solution composition (concentration, pH), process parameters (trans-membrane pressure) and membrane/solution interactions. Experimentally studying all factors affecting rejection by NF for a complex solution would require numerous experiments. Therefore, to save time, a NF simulation software needs to be used.

NanoFlux® is a computer simulation program developed by John Palmeri et al. [59], [60] to model solute transport in NF membranes. It can also be used to characterize NF membrane, pore radius and surface charge density. One of the main benefits of this program is to be able to predict the filtration performance of the membranes for single solutions or complex mixtures of neutral molecules and ions, like sea water or surface water. This program allows one to calculate, starting from standard feed input data, all the necessary NF process output (ionic and molecular rejection, or fluxes,...) from the level of a single membrane element up to that of multi-module, multi-stage plants. It is possible to obtain quick and reliable simulation results by the simultaneous combination of the robust computational algorithms and the internal NanoFlux® database that contains the principal commercial membranes.

NanoFlux® is also easy to use, owing to its well-designed user interface and has been tested and validated using real case studies. With a regularly updated database, it can follow technical demands and commercial market evolution. This modeling program is thus a powerful aid in decision-making and innovation, when it comes to economically choosing the right membrane and optimizing NF processes. It can also be used to minimize significantly difficult and costly pilot studies, thereby reducing the total cost and time needed to choose the appropriate membrane and to scale-up and operate NF plants [61].
1.2.3.3.2 Principle of modeling method

The modeling method used in NanoFlux® is based on an internal database, including information on membrane pore size and membrane-salt pair characterizations. The pore size is estimated from the rejection of model neutral solutes. The membrane-salt pair is characterized by effective membrane charge density (\(X_m\)) and thickness (\(L_{eff}\)) which are optimized by NanoFlux® software via a numerical fitting procedure using the experimental rejection results of single solution of simple salts (NaCl, MgSO₄, Na₂SO₄, CaCl₂).

The calculated rejections are obtained by solving numerically the “Hindered Transport” Extended Nernst-Planck ion flux equations. The best fit parameter values, which minimize the difference between the experimental and theoretical rejections, vary as a function of the salt concentration and pH of the feed. The more accurate these two parameters are, the better the prevision made by the model is [62].

For complex ion mixtures, firstly, the effective membrane charge and effective thickness are determined as a function of feed solution pH, ionic strength and composition using the single salt database combined with an interpolation and weighting scheme. After that, the rejection and solution flux can be well predicted using the internal single salt database.

NanoFlux® can therefore be at the basis of a combined experimental and theoretical method for characterizing, simulating, and optimizing the performance of charged nanofilters.

1.2.3.3.3 Basic equations of NanoFlux®

A theoretical prevision for ionic rejections of multi electrolyte solutions can be provided by the Hindered Electro-Transport (HET) theory which uses the Extended Nernst-Planck (ENP) equation and volume averaged Stokes equation to describe ionic and solution flux through the membrane. These equations were presented in section 1.2.3.2.2.

In NanoFlux®, they are numerically solved using the software internal database – containing values of crystal radius, ionic charge and bulk diffusion coefficients – or a set of user adjustable input parameters:

- \(c_i^f\) the ionic concentration in the feed in mol/L.
- \(X_m\) corresponding to the effective membrane charge density in mol/L
- \(r_p\) the membrane pore radius determined by using a set of standard molecules (sugars and ethylene glycol oligomers).
- \(L_{eff}\) the effective membrane thickness in μm, \(L_{eff} = l_m \left(\frac{\nu}{\tau}\right)\).
the pure water hydraulic permeability (L/h.m².bar),

\[ k_{i}^{res} \] the residual partition coefficient. It is a fitting parameter that can be introduced into the ion partition coefficients, \( k_i \), for certain neutral solutes to account for non-steric interactions (dipole moment-membrane for polar or polarizable solutes, hydrophobic interactions for non-polar ones,...); or for certain ionic species in order to account for exclusion effects other than the electrostatic and steric ones (dielectric,...) [45]. It can be taken from the extended form of equation (1-18) like:

\[
k_i = \frac{c_{im}}{c_i} = k_{i}^{res} \phi_i exp \left(-\frac{z_iF}{RT} \Delta \varphi_D \right)
\]

\[ (1-20) \]

1.2.4 Membrane module and process design

1.2.4.1 Membrane module

A membrane module is the smallest unit of packed membrane area. In order to apply membranes on a technical scale, many modules are normally used to satisfy the technical requirements. The membrane module is the central part of a membrane installation. The module designs depend on two types of membrane configuration: flat and tubular. Plate-and-frame and spiral-wound modules involve flat membranes whereas tubular, capillary and hollow fiber modules are based on tubular membrane configurations. In this part, we focus on just two designs of flat membrane.

The plate-and-frame use flat sheet membranes sitting on a plate that provides a porous support for the permeate outlet. The spiral-wound module uses flat sheets wound around a central tube. The membrane are glued along three sides to form ‘leaves’ attached to a permeate channel along the unsealed edge of the leaf. Thus the packing density of the spiral-wound module is about 500 – 1000 m²/m³ and significantly higher than that of the plate-and-frame. However, the packing density of the spiral-wound module depends very much on the channel height. Feed channel spacers are used in both modules to define the channel height and reduce the effect of concentration polarization. The channel height of these modules is thin, 1 to 3 mm. Permeate spacers are also used to support the membrane from collapsing under pressure and conduct the permeate to the outlet [51].

There are some limitations of the plate-and-frame. The membrane replacement tends to be sheet by sheet which labour intensive is. To obtain the relatively high pressures, the modules tend to have heavy duty end plates and the pressure also constrains the diameter or width of the module. Another is that the plate-and-frame is used for small to medium scale application in
niche areas. The spiral-wound module can be applied on large scales, such as the daily industry and water production. However, they have some drawbacks because of difficult cleaning and high cost [51].

1.2.4.2 Process design

There are two basic operation modes of a membrane system: dead-end mode and cross-flow mode (Figure 1-7). Dead-end mode is the simplest one where all the feed is driven through the membrane while the feed in the cross-flow mode flows parallel to the membrane surface. The dead-end mode can get the high recovery and low energy usage but the flux declines tremendously because of concentration polarization phenomenon and membrane fouling. Furthermore, the increase of rejected component concentrations in the feed causes the quality of the permeate to decrease with time. The cross-flow mode allows a much better fouling control but the recovery is much lower. Flux decline in this case is relatively small and can be controlled and adjusted by proper module choice and cross-flow velocities.

![Schematic drawing of dead-end mode and mode cross-flow of operation](image)

Figure 1-7: Schematic drawing of dead-end mode and mode cross-flow of operation

To take full advantage of cross-flow mode, many kinds of operations are designed for a given module design and feed solution, such as co-current, counter-current, cross-flow and perfect mixing. The schematic of these operations are shown in Figure 1-8. The counter-current flow is the best mode to eliminate the membrane fouling.
In generally, two basic methods which can be used in a single-stage or a multi-stage process are the single-pass system and the recirculation system as Figure 1-9.

In the single-pass system, the feed passes through only one module or many parallel modules without recirculation, hence, the volume of the feed decreases with path length. In a multi-stage single-pass design, this loss of volume is compensated by arranging the modules in a 'tapered design'.
In the recirculation system, a recirculation pump is used to recycle the retentate stream whereas the pressure drop is low. The flow velocity and pressure can be adjusted in every stage. When all of the retentate is recycled, we have a batch process. The batch process can be run continuously until the desired volume reduction factor is reached. This process can generally be used in small-scale applications. When a portion of the retentate is recirculated, we have a feed-and-bleed process.

Depending on the feed quality and the requirements of the permeate quality and capacity of system, we can apply one or many membrane modules in different configurations for a treatment system. The technical parameters of system should be taken into account to obtain an economically viable and sustainable solution.

1.3 Electrodialysis

1.3.1 Principle of electrodialysis

Electrodialysis (ED) is a membrane process in which an electrical potential difference acts as the driving force in order to achieve separation of charged ions from an aqueous solution. It can be used to concentration or removal charged species in feed solution. In this process, the cations migrate from the feed solution towards the negative electrode (the cathode) through the cation exchange membranes which allow only cations to pass. On the other hand, the anions migrate towards the positive electrode (the anode) through the anion exchange membranes. In a conventional process, a large number of alternating cation exchange membranes and anion exchange membranes are stacked together to control the migration of the ions. These membranes are separated by flow spacers which are plastic sheets that allow the passage of water. The streams in alternating flow spacers are a sequence of diluted and concentrated water which flow in parallel to each other [4]. The principle of the electrodialysis process is depicted in Figure 1-10.

Besides, electrolysis occurs at the electrodes, with hydrogen (H₂) and hydroxyl ions (OH⁻) being produced at the cathode. Whereas at the anode, depending on the electrolyte used, chlorine (Cl₂) or oxygen (O₂) and hydrogen ions (H⁺) is produced.

The following electrode reactions may occur:

**cathode:** \[ 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \]

**anode:**

\[ 2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \]

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2e^- \]
1.3.2 Application of ED in desalination

Electrodialysis is one of effective methods for desalination for the production of potable water. Although ED can remove salts from the water with higher concentration of dissolved solids (30 g/L), this technology is generally the most cost effective for the waters with relatively low salt concentrations (less than 5 g/L) mean as brackish water [64][65].

ED has been researched for brackish water desalination application since the 60s [9]. It was used in industry worldwide in many countries, such as American [66], Germany [67], Japan [68] and India [69] in the 80s. Since then the basic process has been significantly modified and developed to satisfy the commercial demands.

In recent years, ED has been integrated with other membrane processes to improve the performance of system and avoid the drawbacks [70], [71]. Abdel-Aal et al. [72] applied ED firstly followed by RO to desalt the Red Sea water. The result showed that this system is economic and cost effective compared with each individual method. When the salinity of sea water was reduced by ED, the energy consumption in RO step was decreased and the recovery was increased. Furthermore, the RO concentrate can be reused as the electrolyte in ED stack. Thampy et al. also observed that the ED-RO hybrid process could avoid a huge water loss while water quality guaranteed [73]. By the way, the integration between NF and ED also gave the higher water recovery and reduced the risk of scaling of sparingly soluble salts [74]. Another
integration method between membranes considered is the feasibility of electrodialysis (ED) on the RO concentrate to reduce the volume of salty water discharge and to improve the water recovery [75], [76]. In addition, Jiang et al. [77] have reported that freshwater and coarse salt can be produced from RO effluent by using ED process.

In an ED process, the electric energy is one of main parts of operation costs. To reduce the water production cost, many researches have been carried out by using renewable energy to apply to an ED process. For example, the electric energy from an off grid wind energy system was used to supply to an electrodialysis desalination plant [78]. The result showed that the ED unit adapted smoothly to variations in wind power to produce a flow 3 to 8.5 m$^3$/h of fresh water with conductivity between 200 and 500 μS/cm and power consumption in the range of 4 to 19 kW. Recently, a novel directly coupled wind–electrodialysis system (wind–ED) with no energy storage was developed [79]. On the other hand, solar energy was also applied to an ED plant by many author [80]–[82]. A good review discussing on the sustainability of integration between electrodialysis and photovoltaic solar energy as the power supply for freshwater production was published by C. F. Gonzalez et al. [83]. The most promising power supply for ED according to [84] is electric solar energy.

1.3.3 Factors affecting the performance of ED in desalination

The performance of ED for desalination is affected by some operating conditions, such as temperature, cell voltage, feed concentration and flow rate of feed solution. Being different with other membrane processes which usually use the performance of rejection to optimize condition of membrane processes, the ED performance can be evaluated by operation time, energy consumption, current efficiency (a measure of how effective ions are transported across the ion exchange membranes for a given applied current) or separation percent (percent of salt removal from water). The effect of the operating conditions is pointed out as follows.

Cell voltage is one of significant factors influencing the performance of ED. The cell voltage was directly proportional to a separation percent when the applied voltage was in the range of 5 – 9 V (lower limiting current). It means that the increase of voltage may get a better separation percent [64]. While the electric energy would be consumed more when cell voltage increases [85]. Besides, the time for desalination remarkably decreased with an increase in cell voltage [8], [85]. Sadrzadeh et al. (2009) studied the effect of cell voltage on the current efficiency in the case of at different flow rate and feed concentrations. The results showed that the increase of the cell voltage (particularly from 4 to 6 V) enhanced the current efficiency at
almost all flow rates and all feed concentrations below 20 g/L corresponding with the studied stack configuration. In cases of the feed concentration over 20 g/L, the cell voltage increase had a negligible effect on the current efficiency at low flow rate (< 1 mL/s). Hence, a slight decrease or increase in the efficiency when solutions with concentration of 20 and 30 g/L were treated was attributed to experimental errors [86]. It can be concluded that the cell voltage increase of the system leads to some benefits, such as increase of the separation percent and the current efficiency and decrease of the operation time. However, the energy consumption increase is a disadvantage.

The effect of feed salt concentration on the performance of the ED process was investigated to determine the scope ED for the range of water salinities. Banasiak et al. reported that the NaCl guideline value for drinking water (500 mg/L) was reached only in the experiments with an initial salt concentration below 10 g/L. With an initial salt concentration of 20, 25 and 35 g/L NaCl, the guideline value was not reached using the same experiment conditions. It was also observed that the increase of feed concentration increased the operation time and after 90–120 min the desalination becomes marginal [8]. Otherwise, the separation percent decreased with a feed concentration increase, in spite of the fact that solution conductivity increased. It was ascribed to concentration polarization phenomenon at high concentrations and limited ion exchange capacity of the membranes [64]. Hence, it was approved that ED is more efficient at lower concentrations.

The effect of the flow rate of the feed solution on ED performance depends on the stack configuration. It was found that the separation percent decreased as the flow rate increased from 0.07 mL/s to 0.22 mL/s (for a stack including one ion exchange membrane pair with the effective membrane area of 60 × 65 mm²). Since a greater flow rate means a lower residence time, ions that were between the membranes did not have enough time to transfer through the membranes [64]. However, Kabay et al. reported that the increase of flow rate from 10 mL/s to 30 mL/s (for a stack including ten ion exchange membrane pairs with the effective membrane area of 1 dm²) did not affect the operation time and the energy consumption of ED process [85]. About the current efficiency, when the flow rate increased it increased to the maximum value and further increasing decreased it.

In addition, temperature, pH and composition of feed solution may also affect ED performance. When the temperature increased, the separation percent decreased. However, greater temperature than 40°C had almost no effect on separation performance [64]. The presence
of divalent ions in feed solution leads to increasing of the operation time, because the transport of
divalent ions through the membranes is lower than that of monovalent ions. Thus, the energy
consumption values were larger for divalent ions than those of monovalent ions [85]. About the
effect of pH, it was obtained that the operation time was shorter at pH 2 than pH 4 and pH 6
when a potential of 5 V was applied (for a stack including ten ion exchange membrane pairs with
the effective membrane area of 1 dm²). However, the effect of pH is negligible at 10 V [87].

1.3.4 Transport in ion-exchange membrane

Electrodialysis is a process in which ions are transported through membranes because of
an applied electrical potential difference. Membranes used are selective for ions, that either
allows the transfer of anions or cations. Ion exchange membranes are fixed charged membranes
containing negatively charged groups or positive charged groups. In neutral membranes, transport
of ions is proportional to the concentration difference, but in ion exchange membranes, it is also
affected by the presence of fixed charges of membrane. The ionic transport through these types of
system is based on two principles: Donnan equilibrium and Nernst – Planck equation.

1.3.4.1 Donnan equilibrium

When an ion exchange membrane contacts with an electrolyte solution, the counter ions
diffuse to membrane due to the concentration difference, while the co-ions are excluded and
cannot pass through the membrane. The electric potential arises between two phases from this
transport of ions and it is called Donnan potential. It can be calculated based on the chemical
potential of the ionic component in the two phases in equilibrium.

In ionic solution, chemical potential of the ionic component is given by:

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \varphi$$

(1-21)

In the membrane:

$$\mu_i^m = \mu_i^0 + RT \ln a_i^m + z_i F \varphi^m$$

(1-22)

where $\mu_i$ is the chemical potential of component i, $\mu_i^0$ is the potential in a given standard state,
$a_i$ is the activity of component i, $z_i$ is the valency of component i, $\varphi$ is the electrical potential, R
is the gas constant, T is the absolute temperature, $F$ is the Faraday constant (1 Faraday = 96500
C/mol) and subscript m denotes membrane.

At the equilibrium, chemical potentials of the ion in two phrases are equal ($\mu_i = \mu_i^m$), thus
$$\Delta \mu_i = RT \ln a_i^m - RT \ln a_i + z_i F (\varphi^m - \varphi) = 0$$

(1-23)
with the equilibrium potential difference $\Delta \varphi_D = \varphi^m - \varphi$

$$\Delta \varphi_D = \frac{RT}{z_i F} \ln \left( \frac{a_i}{a_i^m} \right)$$ (1-24)

for the case of the diluates, the solution is ideal and the ion activity is equal to the corresponding concentration ($c_i$)

$$\Delta \varphi_D = \frac{RT}{z_i F} \ln \left( \frac{c_i}{c_i^m} \right)$$ (1-25)

The Donnan potential gives the potential build-up at the membrane-solution interface when the permeable ions diffuse to the membrane.

### 1.3.4.2 The Nernst–Planck equation

The Nernst–Planck equation describes the flux of ions through an ion exchange membrane under the influence of both an ionic concentration gradient and an electric field.

$$J_i = -D_i \frac{dc_i}{dx} + \frac{z_i F c_i D_i E}{RT}$$ (1-26)

where $J_i$ is the flux of ion $i$ on $x$, $x$ is the axis drawn along a boundary layer, $D_i$ is the diffusion coefficient of ion $i$ (m$^2$/s), $c_i$ is concentration of ion $i$ on $x$, $E$ is the electric field strength.

In cases where ions are transported across a charged membrane without an electro potential difference, such as in NF, RO or UF membranes, a convective term has to be included and the ionic transport is now determined by three contributions, an electrical, a diffusive and a convective term, respectively.

$$J_i = J_{i,dif} + J_{i,elec} + J_{i,conv}$$ (1-27)

This equation is called the extended Nernst-Planck equation in which a convective term is added to equation (1-26). In the absence of coupling phenomena and assuming ideal conditions the extended Nernst-Planck equation can be given as

$$J_i = -D_i \frac{dc_i}{dx} + \frac{z_i F c_i D_i E}{RT} + c_i V$$ (1-28)

where $V$ is the solution velocity vector (m/s).

### 1.3.4.3 Transport number

The current is carried by both ions in an electrolyte solution. However, cations and anions usually carry different portions of the overall current. In ion-exchange membranes, the current is
carried preferentially by the counter ions. The fraction of the current that is carried by a certain ion is expressed by the ion transport number \( t_i \) which is given by:

\[
t_i = \frac{\mu_i}{\Sigma \mu_i} \tag{1-29}
\]

Furthermore, the ion exchange groups fixed in the membrane exclude the co-ions due to the Donnan exclusion, which reduces the diffusion and convection across the membrane. Accordingly, the influence of diffusion and convection to the flux can be neglected [88]. Thus, Equation (1-28) is simplified as:

\[
J_i = \frac{z_i F_\circ \mu_i E}{RT} \tag{1-30}
\]

Substitution equation (1-30) to equation (1-29), we can obtain the transport number as follows:

\[
t_i = \frac{D_i \bar{z}_i \bar{c}_i}{\Sigma D_i \bar{z}_i \bar{c}_i} \tag{1-31}
\]

The transport number is usually related to the permselectivity of membranes. Permselectivity describes the ability of the membrane to pass current solely by means of the counter ions (i.e., ions with charges opposite to those that are bound to the polymer backbone) in the membrane. Thus, a perfectly permselective membrane is one where co-ions (i.e., the ions with the same charge as those that are bound to the polymer backbone) are completely excluded from the polymer matrix and prevented from migrating through the membrane [89].

1.3.5 Membrane process

1.3.5.1 Process parameters

In an ED system, the mass transport through the membranes occurs as long as a direct current is applied. The amount of ion transported is proportional to electric current. The electric current required to remove a number of ions is given by

\[
I = \frac{z_i F Q \Delta c}{\zeta} \tag{1-32}
\]

where \( Q \) is the flow rate (m\(^3\)/h), \( \Delta c \) is the concentration difference between the feed and the diluate (eq/L) and \( \zeta \) is the current utilization. The current utilization is directly proportional to the number of cells in a stack and is governed by the current efficiency.

\[
\zeta = N \eta \tag{1-33}
\]
where $N$ is the number of cell pairs, $\eta$ is the current efficiency.

The electric current is related to the electric potential difference by Ohm’s law:

$$U = R_{st} \cdot I$$  \hspace{1cm} (1-34)

where $U$ is the electric potential difference (V), $I$ is the electric current (A) and $R_{st}$ is the apparent resistance of the total membrane stack (Ω). The value of $R_{st}$ is determined by the resistance of a cell pair $R_{cp}$ multiplied by the number of cell pairs ($N$) in the stack. i.e. $R_{st} = R_{cp} \cdot N$

It is noted that the resistance of a cell pair is the sum of four resistances in series as presented in Figure 1-11.

$$R_{cp} = R_{am} + R_{dc} + R_{cm} + R_{cc}$$  \hspace{1cm} (1-35)

where

- $R_{cp}$ is the resistance of one cell pair (per unit area)
- $R_{am}$ is the resistance of the anion exchange membrane
- $R_{dc}$ is the resistance of the diluate compartment
- $R_{cm}$ is the resistance of the cation exchange membrane
R_{cc} is the resistance of the concentrate compartment.

The electric current is an important parameter of an ED system. The current density also is a main parameter which can be representative for the system. The current density is the electric current applied per unit of membrane area. Increasing the current density leads to an increase in the number of ions transferred. However the current density will reach a limit value when no more ions are available to transfer at the membrane surface. If the limiting current density is exceeded, the process efficiency is drastically diminished because of the increasing electrical resistance of the solution and because of water splitting which leads to both pH changes and additional operational problems. Determination of the current density and the limiting current density is presented in the concentration polarization part.

1.3.5.2 Concentration polarization in ED

In ED, a concentration polarization happens since the selective transport of ions through ion exchange membranes toward the anode or cathode. This transport is the reason why the concentration of counter ions decreases, while the concentration of co-ions increases in the boundary layer of membranes. This phenomenon is denoted as concentration polarization. The concentration polarization also severely affects the economics of process. It was observed that the effect of concentration polarization due to the increase of the co-ion concentration is less severe, although it affects the current utilization to some extent [90]. The decrease in the concentration of counter ions directly affects the limiting current density and increases the electrical resistance of the solution in the boundary layer. Figure 1-12 illustrates the concentration polarization at the surface of a cation exchange membrane with the transport of cations through the membrane.
In turn, applying the Nernst–Planck equation (equation (1-26)) for the transport of cations in the boundary layer and in the membrane gives as follows:

\[ J_+^{bl} = -D_+^{bl} \frac{dc_+}{dx} + \frac{z_+ F c_+ D_+^{bl} E}{RT} \]  

(1-36)

\[ J_m^m = -D_m^m \frac{dc_+}{dx} + \frac{z_+ F c_+ D_m^m E}{RT} \]  

(1-37)

In addition, the current density due to the ion migration in electric field \( (i_{\text{mig}}) \) is given by Ohm’s law:

\[ i_{\text{mig}} = \frac{F^2}{RT} \sum z_i^2 D_i c_i E \]  

(1-38)

Substitution of equation (1-38) and the transport number in equation (1-31) into equation (1-36) in case of the cation transport in the boundary layer, and after rearrangement, the following equation can be derived

\[ J_+^{bl} = -D_+^{bl} \frac{dc_+}{dx} + \frac{t_+^{bl} i}{z_+ F} \]  

(1-39)
and substitution of equation (1-38) and the transport number in equation (1-31) into equation (1-37) in case of the cation transport in the membrane, we also obtain:

\[ J^m_+ = -D^+_m \frac{dc_+}{dx} + \frac{t^m i}{z_F} \]  

(1-40)

The diffusion coefficient of ion in ion exchange membranes is 10 to 10^3 times lower than that in solution [91], hence, the contribution of the diffusive term to the cation transfer in equation (1-40) is low, so that the flux of cations through the membrane is governed mainly by the migration as follows:

\[ J^m_+ = \frac{t^m i}{z_F} \]  

(1-41)

At a steady state the flux of cations through the membrane is equal to that in the boundary layer towards the membrane, i.e.

\[ J^m_+ = \frac{t^b i}{z_F} = -D^b_+ \frac{dc_+}{dx} + \frac{t^b i}{z_F} \]  

(1-42)

Integration of equation (1-42), assuming a constant diffusion coefficient (linear concentration profile) and using the following boundary conditions:

- \( c = c^m \) at \( x = 0 \)
- \( c = c^b \) at \( x = \delta \)

and the following equations can be derived:

\[ c^m_c = c^b_c + (t^m_+ - t^b_+) \frac{i \delta}{z_F D^b_+} \]  

(1-43)

\[ c^m_d = c^b_d - (t^m_+ - t^b_+) \frac{i \delta}{z_F D^b_+} \]  

(1-44)

In these equations, subscript m, bl and b are membrane, boundary layer and bulk solution; \( t^m_+ \) and \( t^b_+ \) are the transport numbers of the cation in the membrane and in the boundary layer; \( c^m_c, c^m_d, c^b_c \) and \( c^b_d \) are the cation concentrations in the concentrate compartment and the diluate compartment at the membrane surfaces and in the bulk solution; \( \delta \) is the thickness of the boundary layer; \( i \) is the current density; \( D^b_+ \) and \( z_+ \) are the diffusion coefficient and electrochemical valence of the cation in solution.
The magnitude of the concentration polarization is largely determined by the current density \(i\). The current density in the boundary layer where ion depletion has occurred can be obtained by rearranging equation (1-44):

\[
i = \frac{D^{b} z_{b} F (c_{b}^{0} - c_{b}^{0})}{\delta (t_{m}^{m} - t_{m})}
\]  

(1-45)

Equation (1-45) shows that when the electrical potential difference is increased, the current density increases, the cation flux increases and consequently the cation concentration decreases. For a given system geometry and feed flow velocity, there is a limiting current density at which the ion concentration in the diluate compartment will approach zero. This limiting current density in the case of a cation permeable membrane is obtained:

\[
i_{\text{lim}} = \frac{c_{b}^{0} D^{b} z_{b} F}{\delta (t_{m}^{m} - t_{m})}
\]  

(1-46)

It can be seen from equation (1-46) that the limiting current density depends on the concentration of cations (ions in general) in the bulk solution \(c_{b}^{0}\) and on the thickness of the boundary layer \(\delta\). In order to minimize the effect of polarization the thickness of this boundary layer must be reduced and hence the hydrodynamics and cell design are very important.

On the other hand, the concentration polarization by the transport of anion through anion exchange membrane also happens in the same behavior that was illustrated for the cation. However, the mobility of anions with the same valence in the boundary layer is a little greater than that of cations. This implies that under similar hydrodynamic conditions for the anion and cation, the limiting current density will be attained faster at a cation exchange membrane than at an anion exchange membrane.

In practical, the limiting current can be determined by plotting \(U/I\) (V/A) versus \(1/I\) (A\(^{-1}\)) [4][92].
1.3.6 Energy consumption in electrodialysis

In electrodialysis, energy consumption is mainly determined by the electrical energy to transfer the ionic components through the membranes and to pump the solutions through the ED unit.

The energy required for the actual desalination process is given by the current passing through the ED stack multiplied with the total voltage drop encountered between the electrodes:

\[ E_{\text{des}} = I \cdot U \cdot t \quad (1-47) \]

where \( E_{\text{des}} \) is the energy consumed in a stack for the transfer of ions from a feed to the concentrate solution, \( I \) is the current passing through the stack, \( U \) is the voltage applied across the stack.

Substitution equation (1-32) and (1-34) into equation (1-47), the required desalination energy is obtained as a function of the stack resistance, the amount of the produced product, the feed and diluate concentration and the current utilization as follows:

\[ E_{\text{des}} = R_{\text{st}} \cdot t \left( \frac{FQ \Delta C}{t} \right)^2 \quad (1-48) \]

The operation of an ED unit requires one or more pumps to circulate the diluate, the concentrate, and the electrode rinse solution through the stack. The energy required for pumping these solutions is determined by the volumes of the solutions to be pumped and the pressure drop. It can be expressed by:

\[ E_p = \eta(Q_d \Delta P_d + Q_c \Delta P_c + Q_e \Delta P_e) \quad (1-49) \]
where $\eta$ is the pump efficiency, $Q$ is the flow rate (m$^3$/s), $\Delta P$ is pressure drop (Pa) and subscripts $d$, $c$ and $e$ denote the diluate compartment, concentrate compartment and electrode compartment, respectively.

So the total energy consumption in ED is:

$$E_{tot} = E_{des} + E_p$$  \hspace{1cm} (1-50)

For an example according to [65], the total energy consumption of an ED unit ranges from 0.7 to 2.5 kWh/m$^3$ for low salinity feed solution (< 2500 ppm), and 2.64 to 5.5 kWh/m$^3$ for a salinity range between 2500 and 5000 ppm, respectively.
Chapter 2

Salt Rejection performance of NF270 membrane
2 Salt Rejection performance of NF270 membrane

2.1 Introduction

Nowadays, nanofiltration (NF) is one of the effective technologies for the treatment of organic and inorganic pollutants in surface and ground waters for drinking water, due to the low osmotic pressure of these feed waters. Furthermore, the low-pressure operation of NF helps increase energy savings with significantly lower installation and operating costs.

As mentioned in Chapter 1, the separation performance of salts by a NF membrane mainly depends on two factors, size exclusion (steric-hindrance effect) and Donnan exclusion (electrostatic effect), since NF membranes are porous membranes and charged on their active pore surface. The weight of these factors on separation performance is different from case to case based on the membrane properties, feed solution composition and operating conditions. Some models were developed to describe successfully the transport of monovalent electrolytes, such as the electrostatic and steric-hindrance (ES) model [93], the Donnan-steric pore model [55], the Teorell-Meyer-Sievers model (TMS), etc. However, experimental data did not fit well with rejection observed for multivalent cations, due to their specific adsorption on the membrane surface, which could reverse the sign of the membrane charge [94]. Thus, a systematic study on the separation performance of a NF membrane should be done in order to have a full understanding of the transport of electrolytes and to predict the membrane performance.

In this chapter, the performance behavior of the NF270 membrane for eliminating salt solutions was evaluated by a series of membrane separation experiments under various feed composition and operating conditions. The studied parameters, including pH, concentration of salted feed solutions and applied trans-membrane, were investigated for their effects on the permeate flux and salt rejection efficiency. The obtained results will serve as a database in the Nanoflux® software to predict the salt rejection by the NF270 membrane.

2.2 Materials and methods

2.2.1 Equipment and filtration protocol

2.2.1.1 Experimental apparatus

Filtration experiments were carried out with a NF pilot presented in Figure 2-1. The membrane was placed inside an Osmonics Sepa CF II cell (Sterlitech Corp., Kent, WA) using flat sheet membrane coupons of 155 cm² (19 cm x 14 cm) in which the effective membrane area was
140 cm². The solution was fed to the SEPA cell by a pump (Cat pump 231) at constant flow of 7.9 L/min from a 10 L feed tank. In order to control water temperature in the feed tank, a circulating thermal bath (A25, Haake, Thermo Scientific) maintained a constant feed water temperature (25 ± 0.5 °C). A valve on the retentate outlet allowed the control of the trans-membrane pressure which was monitored through two manometers located on the inlet and outlet of the cell.

![Diagram](image)

1-Circulating thermal bath, 2- preference thermometer, 3-Feed tank, 4-Temperature probe, 5-Coil, 6-Purge, 7-Three-way valve, 8-High-pressure pump, 9-Manometer, 10-Sepa CF II Cell, 11-Pressure control valve, 12-Balance, 13-Computer

Figure 2-1. Schematic diagram of the NF pilot

### 2.2.1.2 Membrane conditioning

Membrane coupons, after being rinsed several times with deionized (DI) water and wetted completely overnight, were conditioned by the following procedure.

The coupon was placed in the membrane cell with a 65 mil foulant spacer on the feed side and a carrier shim on the permeate side. The feed tank was filled 10 L of pure water and maintained temperature at 25 °C. It was circulated 5 min for stabilization step without applied pressure. Then, the trans-membrane pressure was increased progressively by steps of 2 bar every 5 min from 3 bar until the maximum pressure of 17 bar was reached. This pressure was maintained for 1 h. The value of 17 bar was chosen greater than the maximum pressure used in filtration experiments (15 bar) and lower than the maximum pressure of 40 bar recommended by the manufacturer. After that, the procedure was continued by decreasing pressure from 17 to 3 bar in the same way as done before. The permeate water at every pressure point was weighted when decreasing pressure to calculate pure water flux and membrane permeability.

This conditioning procedure was carried out to eliminate chemical preservation products and compaction effects.
2.2.1.3 Filtration experiment

The feed tank was filled with 10 L of salt solutions with various concentrations and pHs. The membrane coupons after conditioning procedure were installed in the membrane cell with the spacers. Separation experiments in each case were performed at 3, 5, 7, 9, 11, 13 and 15 bar and replicated 2 times. At each pressure point, filtration was stabilized for 5 min before collecting permeate solution for 15 min to calculate the salt rejection and the permeate flux. The salt concentrations were determined in feed and permeate solution in each case by using analytical methods presented in section 2.2.3.

The salt rejection, R, was calculated by the following equation:

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \]  

(2-1)

where R represents the percentage of salt removed (%), and \( C_p \) and \( C_f \) the salt concentration (mol/L) in the permeate and the feed solution, respectively.

The permeate flux at each pressure point was calculated by:

\[ J_p = \frac{m}{d \omega \ t \ A} \]  

(2-2)

where \( J_p \) is the permeate flux (L/m².h), m is the weight of permeate solution collected in a given operating time (g), \( d \omega \) is the density of water at 25 °C (g/L), t is the operating time (h), A is the effective membrane area (m²).

The membrane coupon was used for many experiments until it was broken or fouled. After each experiment the pilot was cleaned repeatedly with DI water until conductivity of the rinsing solution was similar to that of the DI water. Following the cleaning operation, the pure water flux of the membrane coupon was determined again to check whether the membrane was fouled or not (if so it was replaced by a new one).

2.2.2 Membrane NF270

In this study, the NF270 membrane of the Dow Filmtec Company was chosen. The NF270 membrane was designed to treat surface and ground waters with high flux at low operating pressures. The NF270 is considered to be a loose NF membrane while NF90 of the same provider is a tighter one. Manufacturer specifications indicate high rejection of MgSO₄ for both membranes while NaCl is rejected at about 50% for the NF270 versus more than 90% for NF90 [95]. Both are thin film composite (TFC) membranes with a thin active polyamide top layer. The NF270 shows good performance for removing total organic carbon (TOC) and
trihalomethane (THM) at a high percentage. It is also an ideal choice for partial hardness elimination with high flux, resulting in high yields and low energy consumption. The operation with this membrane is more convenient due to high productivity and cleanability in a wide pH range. With these advantages, the NF270 membrane is recommended for use in drinking water production from surface and ground water resources.

The NF270 membrane was characterized by contact angle, zeta potential and pure water permeability. These measurements were performed on membrane coupons after the conditioning procedure.

2.2.2.1 Contact angle

The contact angle is the angle, conventionally measured through the liquid, where a liquid–vapor interface meets a solid surface. It quantifies the wettability of a solid surface by a liquid. When the liquid is water, the water contact angle (WCA) characterizes the hydrophobicity of a membrane surface. Generally, if the WCA is smaller than 90°, the solid surface is considered hydrophilic and if the WCA is larger than 90°, the solid surface is considered hydrophobic [96]. The WCA was determined by the sessile drop method [97]. A 10 μl droplet of distilled water was dropped onto the membrane surface by means of a 50 μl syringe. The angle formed by the drop and the surface of membrane was measured using image analysis software (open source ImageJ software). The contact angle was then determined by interpolation methods (DropSnake plugin method). The measurement was replicated 3 times and the average values are reported.

2.2.2.2 Zeta potential

The zeta potential is the electric potential in the interfacial double layer at the location of the slip plane relative to a point in the bulk fluid away from the interface. The zeta potential characterizes membrane surface charge and is used for quantification of the magnitude of the charge. The zeta potential of membrane was determined with a SurPASS electro-kinetic analyzer (Anton Paar, GmbH) based on the streaming potential method [97]. An adjustable gap cell in which the membrane samples were mounted is about 100 μm height. The electrolyte solution (KCl $10^{-3}$ mol/L) was circulated in the cell between two pieces of membrane. The zeta potential was calculated using the Helmholtz–Smoluchowski equation from the measured streaming current as a function of pH (from pH 3 to pH 10). The pH of the electrolyte was controlled by HCl $10^{-1}$ mol/L and NaOH $10^{-1}$ mol/L solutions. The membrane samples were rinsed and immersed in the electrolyte overnight before the measurement.
2.2.2.3 Pure water permeability

The pure water permeability is defined as the volume of water that passes through a membrane per unit time, per unit area and per unit of trans-membrane pressure. This property characterizes the capacity of a membrane to generate permeate and is an easy way to evaluate the initial performance of a membrane.

In this study, the pure water permeability ($L_p$) was determined by plotting the permeate fluxes as a function of applied pressure as in equation (1-8). $L_p$ is the slope of the linear regression line of the plot.

2.2.3 Salt solutions

The four single salt solutions investigated in this work were NaCl, Na$_2$SO$_4$, CaCl$_2$ and MgSO$_4$, representative of various cation–anion pairs: 1-1, 1-2, 2-1, 2-2, respectively. The feed solutions of these salts were prepared at three different concentrations ($10^{-3}$ mol/L, $10^{-2}$ mol/L and $10^{-1}$ mol/L), except in the case of MgSO$_4$ for which only concentrations of $10^{-3}$ mol/L and $10^{-2}$ mol/L were prepared because of solubility problems at the higher concentration. The diffusion coefficients and Stokes radii of ions determined for these salts are shown in Table 2-1.

Table 2-1: Bulk Diffusion Coefficients and Stokes-Einstein and Pauling Radii of ions [98].

<table>
<thead>
<tr>
<th>Ion</th>
<th>$D_i$ ($10^{-9}$ m$^2$.s$^{-1}$)</th>
<th>Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stokes-Einstein</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.334</td>
<td>0.184</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.792</td>
<td>0.309</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.706</td>
<td>0.347</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>2.032</td>
<td>0.121</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.065</td>
<td>0.231</td>
</tr>
</tbody>
</table>

The effect of pH on the membrane performance was investigated by carrying out filtration experiments at pH 3, 6 and 10. The pH of the feed solutions was adjusted by adding 10% NaOH and 35% HCl solutions for chloride salts. In the case of sulfate salts the 35% HCl solution was replaced by a 9.5% H$_2$SO$_4$ solution. Feed solutions having pH 6 is representative of natural pH and were obtained without adding acid or base.
All inorganic chemicals used were supplied by Sigma Aldrich (ACS reagent grade). The solutions were prepared with the ultra-pure water obtained from a Milli-Q purification system (Merck Millipore, Billerica, MA, USA).

### 2.2.4 Analytical methods

The conductivity of the solutions was measured by a conductimeter Cond 315i (WTW, Germany). Calibration curves obtained at natural pH (Table 2-2) were used to determine single salt concentrations of permeates and retentates obtained by filtration at this pH.

Table 2-2: Calibration curves for measurement of salt concentrations from ion conductivity

<table>
<thead>
<tr>
<th>Salt</th>
<th>Calibration curves ((\sigma_{\text{mS}} = f[C_{\text{mol/L}}])) in the concentration range of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>NaCl</td>
<td>(y = 95.039x + 0.004) (\text{R}^2 = 0.9973)</td>
</tr>
<tr>
<td>Na_2SO_4</td>
<td>(y = 223.29x + 0.0082) (\text{R}^2 = 1)</td>
</tr>
<tr>
<td>CaCl_2</td>
<td>(y = 249.73x + 0.0113) (\text{R}^2 = 0.9999)</td>
</tr>
<tr>
<td>MgSO_4</td>
<td>(y = 211.63x + 0.0074) (\text{R}^2 = 0.9983)</td>
</tr>
</tbody>
</table>

Determination of ion concentration at pH different from natural pH was performed by using an ion chromatograph (IC) system. The IC set-up consisted of an ICS-900 system (DIONEX, USA) with conductivity detector having a resolution 0.0047 nS/cm (DS5, DIONEX, USA).

pH values were assayed with a pH meter, EcoScan pH 6 (Eutech Instruments, Thermo Fisher Scientific Inc., Germany).
2.3 Results and discussion

2.3.1 Membrane characterization

The picture of water contact angle of the NF270 membrane is shown in Figure 2-2. The average value of the water contact angle is $53 \pm 3^0$. This value indicates that the NF270 membrane has a hydrophilic surface. The hydrophilic surface enables the NF270 membrane to be used in water treatment applications easily.

![Figure 2-2: The photo of a water drop on the NF270 membrane surface](image)

The variation of the zeta potentials of NF270 as function of pH in $10^{-3}$ mol/L KCl solution is displayed in Figure 2-3. The isoelectric point of the NF270 membrane was found to be at pH 3.1 in these operating conditions. Hence, the membrane surface is negatively charged when pH is higher than this value. From pH 6, the zeta potential levels off to a value of about -65 mV. On the other hand, at the pH < 3.1, the membrane surface is positively charged. These properties directly affected the salt rejection performances of the membrane, as discussed in following sections.
The plot of the average pure water flux of five measurements versus the applied pressure is presented in Figure 2-4. The linear regression line intercepted 0 because the osmosis pressure in pure water is low. The average water permeability of the NF270 membrane was found to be $15.8 \pm 1.0 \, \text{L/m}^2\cdot\text{h.bar}$ in our conditions of filtration.
2.3.2 Effect of applied pressure on salt rejections and permeate fluxes

The rejection of single salt solutions by NF270 as a function of the applied pressure between 3 to 15 bar at pH 6 is now presented in Figure 2-5. The study was performed with salt solutions at a concentration of $10^{-2}$ mol/L. The rejection increases with increasing applied pressure and levels off at a given rejection depending on the considered salt. These results agreed with the hypothesis that the transport of salt components across the membrane is caused by three mechanisms: diffusion, electrical migration and convection. At 3 bar, the transport of salts is strongly affected by the diffusion mechanism at least for salts slightly and intermediately retained. Hence, salt rejection exhibited its lowest value at low trans-membrane pressure. Once the applied pressure increases, the contribution of the electro-migration and convection to the transport becomes dominant over diffusion and as the result, salt rejection was enhanced. At high applied pressures (13 or 15 bar), the rejection reached a plateau (limiting rejection), where the electro-migration and convection are the main factors of the transport. However, in the case of MgSO$_4$ and Na$_2$SO$_4$, the influence of the diffusion mechanism is negligible because of the high Pauling radius and the low diffusivity of SO$_4^{2-}$ ion. Thus, MgSO$_4$ and Na$_2$SO$_4$ rejections were very high at 3 bar, 92.1% and 85.1% at pH 6, respectively.

![Figure 2-5: The rejection of salt solutions as the function of applied pressure at pH 6](image)

Another point to be mentioned according to Figure 2-5 is that the rejection of salt solutions reached almost a steady state when the applied pressure was higher than 5 bar. For economic reasons, the membrane process could be carried out at medium pressure (5 - 7 bar) with
the same rejection performance. This finding is consistent with the previous investigation of Hilal et al. [99].

Besides, it can be observed that the sequence of rejection was $R_{\text{MgSO}_4} > R_{\text{Na}_2\text{SO}_4} > R_{\text{NaCl}} > R_{\text{CaCl}_2}$ (Figure 2-5). This can be explained by the GCE approximation for the limiting rejection in the HET theory. As mentioned in equation (1-14), the GCE approximation rests on two independent GCE approximations, one for the co-ion Donnan partition coefficient and one for the streaming potential. Firstly, assuming that the normalized membrane charge density ($\xi$) is similar for the four salts, the limiting rejection is mainly affected by the valence and stoichiometric coefficient of ions. It means that in the case of the negatively charged membrane NF270 at pH 6, the limiting rejection should decrease as the cation valence (counter ion) increases and increase as the anion valence (co ion) increases. For example, the rejection of NaCl ($z_1 = 1, v_1 = 1$; $z_2 = 1, v_1 = 1$) is higher than that of CaCl$_2$ ($z_1 = 2, v_1 = 1$; $z_2 = 1, v_1 = 2$). Applying a same calculation for Na$_2$SO$_4$ and MgSO$_4$, we can obtain the following expected rejection sequence: $R_{\text{Na}_2\text{SO}_4} > R_{\text{NaCl}} = R_{\text{MgSO}_4} > R_{\text{CaCl}_2}$. This sequence is in disagreement with the experimental rejection of MgSO$_4$, because the normalized membrane charge density ($\xi$) depends on the salt solution. It can be reinterpreted by using Nanoflux$^\circledR$ modeling.

The rejection of the four salts as a function of the permeate flux for NF270 at concentration of $10^{-2}$ mol/L and their fitted plots by Nanoflux$^\circledR$ is shown in Figure 2-6. It is observed that the experimental rejections are well fitted by the theoretical ones for all studied salts. The residual standard deviations of the experimental and calculated values are 0.00403, 0.00299, 0.00576 and 0.00447, respectively, for NaCl, Na$_2$SO$_4$, CaCl$_2$ and MgSO$_4$. 

![Graph showing rejection performance of NF270 membrane for various salts]
Figure 2-6: The rejection of the four salts as a function of the permeate flux for NF270 at concentration of $10^{-2}$ mol/L at pH 6 (Nanoflux® simulation uses $L_p = 15.8$ L/m².h, $k_t^{res} = 1$ and $r_p = 0.535$ nm)

Depending on these good simulations, the $\xi$ and $L_{eff}$ values for each membrane – salt pair are calculated using Nanoflux® simulation and shown in Table 2-3. The results show that the $\xi$ for the MgSO$_4$ solution is very high in comparison with the three other salts, so that the $k_2^f$ of Mg$^{2-}$ ion (calculated by equation (1-16)) is the smallest. In Table 2-3, the sequence of the Donnan co-ion partition coefficient is $k_{2,NaCl} > k_{2,Na_2SO_4} > k_{2,MgSO_4}$ and the sequence of the rejection hence is $R_{MgSO_4} > R_{Na_2SO_4} > R_{NaCl} > R_{CaCl_2}$ (based on equation (1-15)). This exactly agrees with the experimental rejection, since the influence on rejection of the counter-ion transport number and steric effects are secondary (although non-negligible).

Table 2-3: The normalized membrane charge density ($\xi$) and the effective membrane thickness ($L_{eff}$) for each membrane – salt pair are calculated by Nanoflux® simulation

<table>
<thead>
<tr>
<th>Salts</th>
<th>RSD</th>
<th>$\xi$</th>
<th>$L_{eff}$ (µm)</th>
<th>$k_2^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.00403</td>
<td>-2.9</td>
<td>22.0</td>
<td>0.34</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.00299</td>
<td>-3.6</td>
<td>3.9</td>
<td>0.31</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.00576</td>
<td>-11.5</td>
<td>14.4</td>
<td>0.42</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>0.00447</td>
<td>-20.0</td>
<td>9.0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

\[
y_{NaCl} = 15.533x - 8.3444 \\
y_{Na_2SO_4} = 15.548x - 8.3637 \\
y_{CaCl_2} = 12.128x - 1.8986 \\
y_{MgSO_4} = 12.339x - 8.4072
\]
Figure 2-7: The permeate flux of salt solutions as the function of applied pressure at pH 6.

The relationship between the permeate flux (shorthand for volume flux density) of salt solutions through the NF270 membrane and applied pressure is shown in Figure 2-7. The experiments were carried out with salt solutions at a concentration of $10^{-2}$ mol/L and pH 6 using applied pressures from 3 to 15 bar. The results show that the permeate flux linearly increased with pressure for all studied salt solutions. This trend could be explained by using the equation (1-8) where the solvent flux is directly proportional to the pressure.

In addition, it was observed that salt permeability was dependent on the cation valency and independent of the anion valency: monovalent sodium salts exhibited higher permeate flux than the divalent ones whatever the valency of the counter anion. To explain this observation, it should be recalled that the flux is also affected by osmotic pressure and electro-viscosity effects (as well as other factors, such as concentration polarization, adsorption, gel layer formation and plugging of the pores that are probably negligible here). Since the osmotic pressure of a solution mainly depends on its concentration, the osmotic pressure of the four studied salts is almost similar and the osmotic pressure term in equation (1-8) is small at the concentration of $10^{-2}$ mol/L. Thus the electro-viscosity effect becomes a dominant factor, affecting the slope of the permeate flux vs. pressure curve via the salt permeability (see equation (1-5) and (1-8)).

In equation (1-6) and (1-17), we note that the electro-viscosity coefficient ($\kappa$) and the normalized membrane charge density ($\xi$) are both proportional to the effective membrane charge density ($X_m$). Thus, at constant concentration, an increase in $\xi$ leads to an increase in $\kappa$. As a result, the effective salt permeability, as well as the permeate flux, decreases. As shown in Table 2-3, the normalized membrane charge density $\xi$ for monovalent sodium salts is lower than that of divalent cation salts. This means that the electro-viscosity effect $\kappa$ for them is smaller than that of divalent ones and therefore results in their higher flux in comparison with the others salts (which show an approximately 20% decrease in effective salt permeability).

In addition, the permeate fluxes of salt solutions predicted by Nanoflux® using the specific parameters in Table 2-3 are in good agreement with experiment (Figure 2-8). The actual increase in bulk (dynamic) viscosity (over that of the pure water value) at a salt concentration of $10^{-2}$ mol/L is very small ($< 0.2\%$) and therefore entirely negligible. However, the flux of all studied salts is always lower the pure water flux. This is expected because the osmotic pressure and electro-viscosity effects, due to the presence of salts, resist the transport of water through the membrane.
Figure 2-8: The permeate flux as the function of trans-membrane pressure at pH 6 of salt solutions: a) NaCl, b) Na$_2$SO$_4$, c) CaCl$_2$, d) MgSO$_4$. Nanoflux$^\circledR$ simulation (data experiment): solid blue (star), pure water; solid black (square), salt solution.

2.3.3 Effect of pH on salt rejections and permeate fluxes

To study the effect of pH on the rejection performance of salts by the NF270 membrane, experiments were carried out at 5 bar with salt solutions at concentrations of $10^{-2}$ mol/L at pH 3, 6 and 10. The influence of pH on the rejection of studied salts shown in Figure 2-9 can be explained by the Donnan exclusion theory. Thus, it can be observed that the sequence of rejection was $R_{\text{Mg}^{2+}(\text{MgSO}_4)} \approx R_{\text{Na}^+(\text{Na}_2\text{SO}_4)} > R_{\text{Na}^+(\text{NaCl})} > R_{\text{Ca}^{2+}(\text{CaCl}_2)}$ at pH 6 and pH 10 while at pH 3, the sequence of rejection was $R_{\text{Mg}^{2+}(\text{MgSO}_4)} > R_{\text{Na}^+(\text{Na}_2\text{SO}_4)} > R_{\text{Ca}^{2+}(\text{CaCl}_2)} > R_{\text{Na}^+(\text{NaCl})}$. The Donnan exclusion mechanism suggests that for a single-salt solution, higher the valency of the membrane co-ion higher is its rejection, whereas a higher valency counter-ion leads to a lower rejection of the corresponding salt [100].

The membrane surface was demonstrated to be negatively charged at pH 6 and pH 10, so that the rejection of the counter-ion Ca$^{2+}$ was lower than that of the counter-ion Na$^+$. Conversely, when the pH was shifted to more acidic values (at pH 3), the membrane charge was shifted from...
negative to positive (Figure 2-3), i.e. Ca\(^{2+}\) and Na\(^{+}\) play as co-ions, so that the rejection of Ca\(^{2+}\) was higher than that of Na\(^{+}\) (NaCl). This explanation is confirmed by the GCE results for the HET model, as mentioned above. The Donnan factor in equation (1-14) leads to a high rejection for a binary electrolyte possessing a multivalent co-ion and monovalent counter-ion.

![Figure 2-9: The effect of pH on rejections of cations (a) and anions (b) by NF270 (10\(^{-2}\) mol/L and 5 bar)](image)

However, the rejection of sulfate ion cannot be explained by this theory. In fact, its rejection was still higher than that of chloride at pH 3 (Figure 2-9 (b)), where one might think that sulfate ion would play the role of a membrane counter-ion. Part of the explanation for rejection performance could be steric hindrance and diffusivity effects. The SO\(_{4}^{2-}\) ion is a larger ion than Cl\(^{-}\) ion as seen in Table 2-1 from their respective crystal ionic radii. Hence, its steric
exclusion should be higher whatever the pH. Unfortunately, even the SO$_4^{2-}$ radius is still much smaller than the pore size and therefore steric effects cannot provide the principal explanation. A more plausible explanation can be found by noting the high flux for Na$_2$SO$_4$ at pH 3 (see below): this result suggests that the effective membrane charge remains negative, despite the low pH value, and moderate in absolute value in this case, leading to relatively weak electro-viscosity effects.

Otherwise, the rejection of the Mg$^{2+}$ ion (in MgSO$_4$) is higher than that of the Na$^+$ ion (in Na$_2$SO$_4$) at all pH, although it is smaller than Na$^+$ ion in crystal radius and hence smaller steric hindrance. Besides, if these cases obeyed the GCE model, the Mg$^{2+}$ rejection would be higher than the Na$^+$ rejection at pH 3 and the contrary at pH 6 and 10. This complication comes from the effective membrane charge density varying with salt, as described in the previous section for pH 6, an effect corroborated by the measured fluxes as a function of pressure. As seen in the figure below, the permeate flux for MgSO$_4$ is lower than the other salts likely indicative of a higher $\xi$ value.

![Figure 2-10: The effect of pH on the permeate flux for different salt solutions (10-2 mol/L and 5 bar)](image)

The effect of pH on the permeate flux through the NF270 membrane is shown in Figure 2-10. It is observed that the permeate flux decreases when the pH is shifted to more alkaline values for all of the four salts studied. This is attributed to the increase of absolute value of the effective membrane charge density at higher solution pH. This increase causes an increase of the
electro-viscosity coefficient and a decrease of the salt solution permeability. As a result, the permeate flux decreases when the pH increases.

2.3.4 Effect of feed concentration on permeate fluxes and salt rejections

The relationship between the permeate flux of salt solutions through the NF270 membrane and feed concentration is shown in Figure 2-11. The experiments were carried out with salt solutions at concentration of $10^{-3}$ mol/L, $10^{-2}$ mol/L and $10^{-1}$ mol/L at pH 6 over the same range of applied pressure. Generally, the permeate flux decreases when the feed concentration goes up for all of the four salts studied. This trend was attributed to the increase of osmotic pressure $\Pi$ with increasing salt concentration (Table 2-4). Especially, the fluxes of CaCl$_2$ and Na$_2$SO$_4$ solutions were highly reduced by increasing the concentration to $10^{-1}$ mol/L. Actually, the effective osmotic pressure $\Pi_{eff}$ is the osmotic pressure corrected by the salt rejection at the given applied pressure $R_{\Pi}$ according to the following equation:

$$\Pi_{eff} = \Pi \times R_{\Pi}$$  \hspace{1cm} (2-3)

From rejection at a pressure of 5 bar reported in Figure 2-12 for NaCl (0.34) and CaCl$_2$ (0.36) and assuming that of Na$_2$SO$_4$ might be about 0.85, $\Pi_{eff}$ values were calculated to be 1.6, 2.4 and 6.2 bar, respectively. These data clearly explain why there was no measurable flux for CaCl$_2$ and Na$_2$SO$_4$ at 3 bar and at 3 and 5 bar, respectively, since their effective osmotic pressures at a concentration of $10^{-1}$ mol/L are higher than the applied pressure.

As mentioned in section 2.3.2, the flux is dependent on the cation nature. Therefore, the order for the highest flux observed was Na$_2$SO$_4 >$ CaCl$_2 \approx$ MgSO$_4$ with values of 244, 200 and 196 (L/m$^2$.h), respectively, at a concentration of $10^{-3}$ mol/L, where the osmotic pressures are the smallest.
Figure 2-11: Effects of feed concentration on the permeate flux for different salts (a) NaCl, (b) \( \text{Na}_2\text{SO}_4 \), (c) CaCl\(_2\) and (d) MgSO\(_4\) (pH 6)

Table 2-4: The osmotic pressure and ionic strength of salt solutions in different concentration

<table>
<thead>
<tr>
<th></th>
<th>( \Pi ) (bar)</th>
<th>I (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NaCl} )</td>
<td>( C^* ) (mol/L)</td>
<td>0.001</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_4 )</td>
<td>0.058</td>
<td>0.43</td>
</tr>
<tr>
<td>( \text{CaCl}_2 )</td>
<td>0.076</td>
<td>0.77</td>
</tr>
<tr>
<td>( \text{MgSO}_4 )</td>
<td>0.064</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>0.049</td>
<td>0.47</td>
</tr>
</tbody>
</table>

\( C^* \) is an approximate concentration while \( \Pi \) and I were calculated with the actual concentration.

The effect of feed concentration on rejection performance is shown in Figure 2-12. The rejection of salts tends to decreases with increasing concentration. This can be illustrated, for example, by considering the limiting rejection obtained in the GCE approximation. A decrease of
the normalized membrane charge density with increasing feed concentration (equation (1-17)) leads to a higher transmission, because of an increase of the Donnan co-ion partition coefficient (equation (1-16)), and therefore a lower salt rejection. This trend can be clearly seen in the NaCl filtration case (Figure 2-12(a)). The NaCl rejection reached 85, 78 and 53 % at 15 bar at a concentration of 10^{-3} \text{ mol/L}, 10^{-2} \text{ mol/L} and 10^{-1} \text{ mol/L}, respectively.

![Figure 2-12: Effects of feed concentration on salt rejections: (a) NaCl, (b) Na_{2}SO_{4}, (c) CaCl_{2} and (d) MgSO_{4} (pH 6)](image)

Otherwise, it can be seen in Figure 2-12 (b-d) that the rejection for the three other salts is quite similar when the feed concentration increases. The highest rejection was for MgSO_{4} solution, followed by the Na_{2}SO_{4} and CaCl_{2} solutions, with the highest values of 98, 97 and 65%, respectively. Actually, the increase of the feed concentration also leads to an increase in the effective membrane charge density, although the normalized membrane charge density generally decreases. The rate of increase of the membrane charge density varies with salt type. Thus, the
similar salt rejections observed in the case of Na$_2$SO$_4$, CaCl$_2$ and MgSO$_4$ may come from a near equality between the increase in membrane charge density and concentration, leading to a nearly constant value of normalized membrane charge density.

As stated above, the sieving mechanism, even for SO$_4^{2-}$ ions with a large crystal radius, is not the dominant exclusion mechanism. Hence, it is possible that an increase in the effective membrane charge with increasing salt concentration for Na$_2$SO$_4$ and MgSO$_4$ leads to only a slight influence on their rejection.

In the case of CaCl$_2$ filtration at a concentration of $10^{-3}$ mol/L, the rejection appears to be governed mainly by the Donnan exclusion and was demonstrated to be lower than that of NaCl. When the concentration is increased, it is expected that rejection will decrease, due to the decrease of the normalized membrane charge density. However, this expectation is contradicted by experiment: the rejection was almost similar when the concentration of CaCl$_2$ increased. Such a result in the context of rejection by Donnan exclusion has been explained by Peeters et al. [94]: an increase in the divalent cation concentration may cause an increase in effective membrane charge by ion adsorption on or in membrane. For the NF270 membrane we suggest another mechanism for CaCl$_2$: it could be that the effective membrane charge density changes sign at high salt concentration, going from negative to positive with an amplitude such that the rejection of the membrane co-ion Ca$^{2+}$ remains roughly constant by Donnan exclusion.

This mechanism could explain the observed phenomenon that the sequence $R$(NaCl) > $R$(CaCl$_2$) at the lower concentrations of $10^{-3}$ mol/L and $10^{-2}$ mol/L (negatively charged membrane) was inverted at the higher concentration of $10^{-1}$ mol/L (positively charged membrane). A similar phenomenon has also been reported by Wang et al. [100]. This possibility can be tested by modeling the solution flux as a function of salt concentration, as was done for $10^{-2}$ mol/L. This study is currently underway. Another possibility is that non-electrostatic and non-steric exclusion mechanisms may play an important role (for example, dielectric ones). Although this possibility is outside the scope of the present thesis, it is currently under study.

2.4 Conclusions

In this study, filtration experiments of the four representative single salts by the NF270 membrane were carried out under different operating conditions on a laboratory-scale pilot. These experiments have brought a deeper understanding of the influence of operating conditions to the membrane performance. Depending on the obtained results, we can conclude as follows.
The NF270 membrane is a polymeric membrane with a hydrophilic surface which is negatively charged at pH > 3.1. The NF270 membrane had a high water permeability, 15.8 (L/m\(^2\).h.bar), thus it could present a high flux at low pressure. The salt rejection performance of NF270 showed that this membrane is promising for use in the desalination of brackish water with an acceptable rejection and the high flux at low pressure.

The flux performance of NF270 depends on trans-membrane pressure, osmotic pressure as well as electro-viscosity effect. The changes of operating conditions or feed composition will affect these factors and result in the change of flux. For instance, when the applied pressure increases, the flux will increase; furthermore the increase of osmotic pressure with increasing feed concentration will reduce the flux.

On the other hand, at pH 6 the monovalent sodium salts showed higher permeate flux than the divalent ones whatever the valency of the counter anion. It was attributed to the increase of electro-viscosity effect due to the increase of normalized membrane charge density at a constant concentration.

The effect of pH on the flux is mainly relative to the change of effective membrane charge density by pH. An increase in the amplitude of the membrane charge density at higher pH leads to a reduction in permeate flux. Another possibility is that in certain cases the membrane charge density changes sign for low pH and/or high salt concentration (in the case of CaCl\(_2\), for example).

The rejection performance of NF270 depends on a complex combination of many factors, such as diffusive flow, convective flow, electric migration flow, as well as ion size (sieving exclusion) and electrostatic interactions between the membrane and ions (Donnan exclusion).

The effect of applied pressure on the rejection performance is a good evidence for the distribution of diffusive and convective flows as well as electrical migration on the transport of salt through the membrane. At low applied pressure (3 bar), the transport of salts is mainly caused by diffusion, so that the rejection was low (such as rejection of NaCl and CaCl\(_2\)) and significantly affected by ion size (such as rejection of Na\(_2\)SO\(_4\) and MgSO\(_4\)). Once the applied pressure increases, the contribution of convection and electro migration to the transport increases and as a result, the rejection of salts increased. At high applied pressures (13 or 15 bar), the rejection leveled off to the maximum value. In this case, the convection and electro migration are a main factor of the transport.
The effect of pH on the rejection can be explained by Donnan exclusion because increasing the pH beyond 6 reduces the change of membrane zeta potential. For instance, the rejection of Ca\(^{2+}\) ion was lower than that of Na\(^{+}\) ion at pH 6 and pH 10 where the membrane surface is negatively charged. Conversely, at pH 3, the membrane surface is positively charged, and the rejection of Ca\(^{2+}\) ion was higher than that of Na\(^{+}\) ion.

However, the Donnan effect becomes less important for the ions which have large size and low diffusivity. For example, the rejection of SO\(_4^{2-}\) ion was higher than that of Cl\(^{-}\) ion at pH 3 although SO\(_4^{2-}\) and Cl\(^{-}\) ions are membrane counter-ions and SO\(_4^{2-}\) ion has a higher valency. This is caused by the sieving effect of the larger SO\(_4^{2-}\) ion. In contrast, the complication of the rejection behavior of the Mg\(^{2+}\) ion (in MgSO\(_4\)) in comparison with that of the Na\(^{+}\) ion (in Na\(_2\)SO\(_4\)) can be explained by the variation of effective membrane charge density with salt. For instance, at pH 6 the rejection of the Mg\(^{2+}\) ion is expected to be lower than that of the Na\(^{+}\) by Donnan exclusion. Nevertheless, its rejection was higher than that of the Na\(^{+}\) ion, due to the high normalized membrane charge density for MgSO\(_4\) in comparison with that for Na\(_2\)SO\(_4\).

The GCE approximation can also be used to illustrate and explain the effect of feed concentration on rejection performance: a decrease of the normalized membrane charge density, \(\xi\), with increasing feed concentration causes a reduction of salt rejection. However, the decrease of \(\xi\) may be different with salt, because of the concomitant increase in the membrane charge density with the increasing concentration. Two concomitant increases lead to a constant \(\xi\) as the function of concentration, and therefore the salt rejection in case of Na\(_2\)SO\(_4\), CaCl\(_2\) and MgSO\(_4\) is nearly independent of salt concentration.

The possibility that non-electrostatic and non-steric exclusion mechanisms, such as dielectric ones, for example, may play an important role cannot be ruled out and this is currently under study.
Chapter 3

Removal of pesticides used in the Mekong Delta by nanofiltration
3 Removal of pesticides used in the Mekong Delta by nanofiltration

3.1 Introduction

The Mekong Delta is the most downstream part of the Mekong River Basin. There is an abundant surface water resource flowing through an interlacing network of rivers and canals to supply for the irrigation of crops, aquaculture and also for daily domestic uses, including for drinking water. However this water resource is faced with many environmental problems, such as flooding, drought, climate change inducing less rain fall and salinity intrusion [11], [12], [30]. Especially, pesticide pollution is one of the major problems. A detailed review of the occurrence pesticide pollution in surface water in the MD was introduced in section 1.1.5.6.

The use of surface water following a primary treatment which is common performed in rural areas is a potential threat for human health. Toan et al. [2] proved that the simple treatment used for preparing drinking water (flocculation followed by boiling) was inefficient for removing present pesticides. The concentration of some of them even increased because of the boiling step. In addition, some pesticides were also detected in some purchased bottled water at concentrations exceeding the guideline values of the European Commission on drinking water [1]. Thus more effective water treatment methods need to be implemented at the household level, as well as in water treatment plants.

Treatment of pesticides in water became a concern at the beginning of 1960s. Many methods were studied and applied to eliminate them, such as adsorption [101]–[103] or advanced oxidation processes [104], [105]. However, they met some obstacles relating to the saturation of adsorbents as well as the presence of toxic chemical by-products in the oxidation processes [44]. In this context, NF might be one of the most appropriate methods for the removal of pesticides with not only high efficiency, but also low energy consumption in a comparison with other pressure-driven membrane processes. Several research groups have systematically studied the retention of pesticides by NF membranes and the related articles have been reviewed in recent papers [44], [106].

On the other hand, the removal of solutes by NF is achieved by two main exclusion mechanisms: size exclusion and Donnan exclusion. Size exclusion or sieving is based on the relation between the pore size of the membrane and the size of permeating molecules. In contrast, Donnan exclusion is based on with the interaction between the membrane surface charge, solute charge and polarity. On the other hand, the adsorption of pesticides on membrane surfaces is one of the important factors that can influence their rejection [106], [107]. The pesticide molecule
adsorbed on a membrane surface can be transported through the membrane more easily, entailing a reduction of its rejection. More adsorption corresponds to a lower rejection. The adsorption has been demonstrated to be controlled by the hydrophobicity of the pesticide and also by its dipole moment [108]–[110]. Especially in the case of pesticide mixtures, the competitive adsorption of pesticides on membrane can drastically affect the removal efficiency.

In addition, the presence of inorganic ions has been identified as having an influence on pesticide rejection [107]. This effect is different for each case, which can be either negative or positive, depending on the membrane used, the ions present and their concentration. Different hypotheses have been proposed to explain the observations. For example, in the presence of an intermediate sodium chloride concentration (2.5 mM), rejection of atrazine, isoproturon and prometryn slightly increased for three Dow Filmtec membranes (NF270, NF90 and XLE). It was attributed to a pore blocking effect or a narrowing the pores by the ions [111], [112]. When the NaCl concentration was increased to 5.2 mM [111] or even 100 mM [113], the rejection tended to be reduced for all pesticides and membranes used. The hypotheses which have been formulated in these cases were a swelling of the membrane pores, a decrease of the solute hydrodynamic radius or a combination of the two phenomena. In other examples, the presence of the calcium ion might induce an increase of rejection by the pore blocking effect [107] or a reduction of removal efficiency by the Donnan effect [111].

Therefore, the need for systematic studies of the effect of adsorption, the presence of inorganic ions and other parameters on the rejection of pesticide is evident. The aim of this chapter was to investigate the efficiency of two NF membranes, NF90 and NF270, to remove some frequently detected pesticides in the surface water of the Mekong Delta. Fenobucarb (Fen), isoprothiolane (Iso), and pretilachlor (Pre) were chosen as the most representative pesticides occurring in this area. The adsorption of pesticides used on the membranes was studied systematically to understand its effect on rejection. Synthetic river water samples containing salt concentration similar to those encountered to real river water were used to investigate the influence of salts on the rejection.

### 3.2 Materials and methods

#### 3.2.1 Membrane selection and characterization

Two kinds of flat-sheet-type NF membranes NF270 and NF90 were used in this study. These are popular membranes commercially available from Dow Filmtec and useful for
removing organic compounds, as well as salinity in water. Characterization of the membranes was carried out by measuring contact angle, zeta potential and pure water permeability. These measurements were performed on membrane coupons after cleaning and conditioning procedures like those presented in Chapter 2 (section 2.2). Contact angle was measured by a lab-made setup. Zeta potential was determined at pH 7 and 30µS/cm KCl solution (PAAR EKA-ElectroKinetic Analyzer RV. 4.0). Pure water permeability was determined with Milli-Q water using the procedure same as in section 2.2.2.3.

The characteristics of the membrane were shown in Table 3-1. The values reported for permeability were averages of all the experiments done for each membrane. Both NF270 and NF90 have polyamide thin-film composites on the top layer. The NF270 membrane was less compact with looser pores (higher MWCO) than NF90, so it had a higher water flux and a lower salt rejection. The small difference of contact angle for the two membranes showed that NF90 was somewhat more hydrophobic than NF270. These characteristics will affect the separation and adsorption properties of the membranes.

### Table 3-1: The characteristics of the membrane used in this study

<table>
<thead>
<tr>
<th></th>
<th>NF270</th>
<th>NF90</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCO (Da, 30°C)(^a)</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Membrane materials of the filtration layer</td>
<td>polyamide</td>
<td>polyamide</td>
</tr>
<tr>
<td>Contact angle (°)(^b)</td>
<td>53±3</td>
<td>68±2</td>
</tr>
<tr>
<td>NaCl rejection (%)(^c)</td>
<td>50</td>
<td>90−96</td>
</tr>
<tr>
<td>Average pore size (nm)(^d)</td>
<td>0.38</td>
<td>0.31</td>
</tr>
<tr>
<td>Pure water permeability (L/h·m(^-2)·bar(^-1))(^b)</td>
<td>17.0±1.3</td>
<td>9.0±1.1</td>
</tr>
<tr>
<td>Zeta potential at pH 7 (mV)(^b)</td>
<td>-66</td>
<td>-25</td>
</tr>
</tbody>
</table>

\(^a\) Molecular weight cut-off, values obtained from Ref. [114].
\(^b\) Experimental values determined in this study.
\(^c\) From the manufacturer [95]
\(^d\) Values obtained from Ref. [115].

#### 3.2.2 Target pesticides

The three target pesticides were purchased from Sigma Aldrich and used as received: fenobucarb (purity 97.0%), isoprothiolane (purity 98%) and pretilachlor (purity 98.7%). Single standard stock solutions with a concentration of 1000 mg/L were prepared for each pesticide in
acetonitrile/water (1/1) and stored at 4°C. The single pesticide feed solutions were prepared by
dilution of stock solution with ultra-pure water at a concentration of about 300µg/L for
fenobucarb and isoprothiolane, and about 1000µg/L for pretilachlor (for reasons of detection). A
mixture of three pesticides was prepared at a concentration similar to that of each compound in
single solutions by diluting individual standard solutions with ultra-pure water. The feed
solutions were used at natural pH (5.9-6.2).

3.2.3 Synthetic Mekong river waters

For the study of the influence of coexisting inorganic salts in feed solutions on the
rejection of pesticides, two synthetic model waters representative of surface water in the MD
were prepared. They are corresponding with the maximum value and the median value of
chloride ion concentration found during the dry season in the salinity intrusion region. Since the
data of monitoring program included only results for anions (Cl\(^-\), SO\(_4^{2-}\)), cation (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\))
concentrations of the synthetic samples were calculated based on the charge balance of cations
and anions in solution and the relative mass ratios of cations in some representative samples in
the Mekong River. The respective ratios of cations were calculated from their average
concentration in ten river samples in the salinity intrusion region. The composition of water
samples and the ratio of cations are shown in Table 3-2.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mass ratio of cations (%)</th>
<th>Maximum(^*) (mg/L)</th>
<th>Median(^*) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td></td>
<td>13887</td>
<td>3184</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td></td>
<td>1763</td>
<td>449</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>83.4</td>
<td>7316</td>
<td>1693</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>3.38</td>
<td>297</td>
<td>68.6</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>13.2</td>
<td>1160</td>
<td>268</td>
</tr>
</tbody>
</table>

\(^*\) Maximum and median designate the synthetic solutions containing salts at the maximum value and the median value.

According to Table 3-2, two synthetic solutions were prepared with the following
compositions, respectively:
- 16.36 g/L of NaCl, 2.608 g/L of Na$_2$SO$_4$, 1.091 g/L of CaCl$_2$.2H$_2$O, 9.812 g/L of MgCl$_2$.6H$_2$O and a mixture of pesticides, including 300 ppb of fenobucarb, 300 ppb of isoprothiolane and 1000 ppb of pretiachlor.

- 3.767 g/L of NaCl, 0.664 g/L of Na$_2$SO$_4$, 0.247 g/L of CaCl$_2$.2H$_2$O, 2.238 g/L of MgCl$_2$.6H$_2$O and a mixture of pesticides with the same concentration as above.

All of the inorganic salts used in this study were supplied by Sigma Aldrich (ACS reagent grade).

### 3.2.4 Analytical methods

The pesticide concentrations were analyzed by direct injection liquid chromatography with the tandem mass spectrometry method (DI-LC/MS/MS). The chromatography was achieved using a Waters HPLC 2695 (Waters, UK). The MS/MS detector was equipped with a Waters Micromass Quattro Micro mass spectrometer (Waters, UK) with an electrospray ionization (ESI) interface in positive mode using multiple reaction monitoring (MRM) with two mass transitions. The pesticide separation was performed on a C18 column (UP5ODB-15QS, 4.6 mm * 250 mm, 5 µm particles) with an injection volume of 5 µl. The flow of the water – acetonitrile (15:85, v/v) mobile phase was 0.2 ml/min. The optimized mass spectrometric parameters were the following: capillary potential 3.5 kV, cone voltage 20 V, extractor 3 V, source temperature 120°C, desolvation temperature 450°C, cone gas flow 50 L/h, and desolvation gas flow 500 L/h. Nitrogen was used as nebulizer gas and argon as collision gas. The calibration curves were made in a concentration range from 1600 µg/L to 9 µg/L for each pesticide in the two different matrices (with and without salts) to avoid matrix effects on results. The limit of detection and MS quantification parameters of each pesticide are shown in Table 3-3.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Retention time (min)</th>
<th>Precursor ion (m/z)</th>
<th>Fragment ion (m/z)</th>
<th>Cone (V)</th>
<th>Collision energy (V)</th>
<th>LOD (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenobucarb</td>
<td>1.22</td>
<td>208.2</td>
<td>94.8</td>
<td>20</td>
<td>10</td>
<td>3.2</td>
</tr>
<tr>
<td>Isoprothiolane</td>
<td>1.34</td>
<td>291.1</td>
<td>230.6</td>
<td>17</td>
<td>12</td>
<td>2.9</td>
</tr>
<tr>
<td>Pretiachlor</td>
<td>1.73</td>
<td>334</td>
<td>256.2</td>
<td>30</td>
<td>14</td>
<td>33</td>
</tr>
</tbody>
</table>
Chapter 3 || Removal of pesticides used in the Mekong Delta by nanofiltration

The determination of anions and cations in the feed solution and the permeate was performed by ion chromatograph (ICS-900, Dionex). The conductivity of the samples was measured with a conductivity meter Cond 315i (WTW, Germany).

3.2.5 Sorption studies

3.2.5.1 Sorption experiment protocol

The experiments were carried out using the following procedure: 100 mL of single pesticide solutions at a given concentration or of mixtures was stirred in a glass bottles with a 3 cm\(^2\) piece of membranes at room temperature. The surface area was taken in proportion to the ratio between the effective membrane area and the volume of filtered feed solution in separation experiment. Prior to the sorption experiment, each membrane was cleaned and conditioned according to the procedure used in filtration (section 2.2.1). After the desired time of equilibrium, the concentration of pesticides in solution was measured and the adsorbed amount of pesticide adsorbed by the membrane was determined by the following equation:

\[
Q = \frac{(C_0 - C_e) \times V}{S}
\]  

(3-1)

where \(Q\) is the amount of pesticide adsorbed per unit area of membrane (µg.cm\(^{-2}\)); \(C_0\) is the initial concentration of pesticide (µg. L\(^{-1}\)); \(C_e\) is the concentration of pesticide in solution at the equilibrium time (µg.L\(^{-1}\)); \(V\) is the solution volume (L); and \(S\) is the area of membrane used (cm\(^2\)).

3.2.5.2 Effect of time on the adsorption

The effect of time on the adsorption of pesticides was investigated as described in the sorption protocol. Single pesticide solutions of 300 µg/L isoprothiolane, 300 µg/L fenobucarb, 1000 µg/L pretilachlor or the mixtures were stirred with membranes for 2, 4, 8, 24, 48 and 72 h.

3.2.5.3 Adsorption isotherm

Solutions of different initial concentrations – 30, 300, 1500 µg/L for fenobucarb, and isoprothiolane and 100, 1000, 5000 µg/L for pretilachlor – were used to investigate the effect of concentration on the pesticide adsorption by 3cm\(^2\) of membrane in 100 ml of solution for 48 h.
3.2.6 Equipment and filtration protocol

3.2.6.1 Experimental apparatus

The experimental apparatus used in these experiments was essentially the same as that shown in section 2.2.1.1. There were, however, some modifications necessary for the experiments with pesticide. All of parts of the pilot were made from stainless steel 316 to reduce the adsorption of pesticide compounds from the feed solution. The feed tank was 5 L.

3.2.6.2 Separation experiment protocol

Our standard protocol for NF experiments included four steps. At first, the membrane was rinsed with DI water several times and afterwards was immersed in DI water overnight. Secondly, membrane conditioning with DI water was carried out to eliminate chemical preservation products and compaction effects. The coupon was placed in the membrane cell and the pure water was circulated by increasing pressure by steps of 2 bar every 5 min from 3 bar until reaching the maximum pressure of 15 bar, which was kept for 1 h. This pressure was chosen greater than the maximum pressure used in filtration experiments (11 bar) and lower than the maximum pressure of 40 bar recommended by the manufacturer. After that the applied pressure was decreased from 15 bar to 3 bar in the same way. The pure water permeability was determined from these experiments.

In the third step, the feed tank was filled with 5 L test solutions. All separation experiments for each kind of membrane or each kind of test solution were performed at 5, 7, 9 and 11 bar, over 30 min, repeated 2 times. The feed solution was at natural pH (5.9 – 6.2), while the temperature was maintained at 25°C to avoid its influence on the flux and rejection of solutes. The concentrations of pesticides were measured for feed and permeate solutions to calculate the rejection for every experiment. The rejection, R, was calculated by the following equation:

\[
R = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

where R represents the percentage of pesticides removed (%), and \(C_p\) and \(C_f\) the concentration of pesticides (µg/L), respectively, in the permeate and the feed solutions.

The fourth step included cleaning the pilot after termination of the experiment. The whole experimental apparatus was washed with acetone and repeatedly rinsed with DI water. Following the cleaning procedure, the membrane coupon was placed back to determine again the pure water
flux. Reduction of pure water flux was determined as a percentage of clean water flux before and after membrane operation as follows:

\[
FR_{PW} = \frac{J_{Wa} - J_{Wb}}{J_{Wb}} \times 100
\]

(3-3)

where \(FR_{PW}\) is reduction of pure water flux (%); \(J_{Wb}\) and \(J_{Wa}\) are the initial and the final pure water flux (L.h\(^{-1}\).m\(^{-2}\)).

A virgin membrane coupon was used for each new experiment to make sure that pesticide sorption on membrane surface did not impact the rejection results.

### 3.3 Results and discussion

#### 3.3.1 Target pesticide properties

Fenobucarb, isoprothiolane, and pretilachlor are representative of the three main kinds of pesticides used in the Mekong Delta, depending on their function: insecticide, fungicide and herbicide. They have been detected with a great frequency in surface water [2]. The molecular structure and physicochemical properties of the pesticides are presented in Table 3-4. All pesticides are hydrophobic (logK\(_{ow}\) > 2), moderately soluble in water, except fenobucarb. The dipole moment of isoprothiolane is higher than that of fenobucarb and pretilachlor.

The diffusivity and the size of solutes are two important parameters required to understand and predict the rejection in NF. The diffusion coefficient (m\(^2\).s\(^{-1}\)) can be calculated using the Wilke-Change correlation [116] given by:

\[
D_s = \frac{7.4 \times 10^{-12}(\varphi M_w)^{0.5}T}{\eta V_s^{0.6}}
\]

(3-4)

where \(\varphi\) is an association factor for the solvent (\(\varphi = 2.6\) for water), \(M_w\) is the molecular weight of the solvent (\(M_w = 18\) g/mole for water), \(\eta\) is the viscosity solvent (cp) and \(V_s\) is the molar volume of the solute at normal boiling point (cm\(^3\). mol\(^{-1}\)). The molar volume of the solutes is estimated from the group contributions of structural contributions to molar volumes [116]. Stokes radii \(r^S\) of the three pesticides can be then determined using the Stokes–Einstein equation:

\[
r^S = \frac{10^9k_BT}{6\pi\eta D_s}
\]

(3-5)

where \(r^S\) is the molecular radius or Stokes radius (nm), \(D_s\) is the diffusion coefficient of the organic compound in water (m\(^2\).s\(^{-1}\)), \(k_B\) is the Boltzmann constant (J.K\(^{-1}\)), \(T\) is the absolute temperature (K), and \(\eta\) is the viscosity of water (N.s.m\(^{-2}\)).
Chapter 3 || Removal of pesticides used in the Mekong Delta by nanofiltration

Table 3-4: The molecular structure and physicochemical properties of the target pesticides

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Fenobucarb</th>
<th>Isoprothiolane</th>
<th>Pretilachlor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Fenobucarb" /></td>
<td><img src="image" alt="Isoprothiolane" /></td>
<td><img src="image" alt="Pretilachlor" /></td>
</tr>
<tr>
<td>Molecular formula</td>
<td>(C_{12}H_{17}NO_2)</td>
<td>(C_{12}H_{18}O_4S_2)</td>
<td>(C_{17}H_{26}ClNO_2)</td>
</tr>
<tr>
<td>Use (^b)</td>
<td>Insecticide</td>
<td>Fungicide, insecticide</td>
<td>Herbicide</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>207.3</td>
<td>290.4</td>
<td>311.8</td>
</tr>
<tr>
<td>Solubility (20°C) (mg/L) (^a)</td>
<td>420</td>
<td>54</td>
<td>50</td>
</tr>
<tr>
<td>(\log K_{ow} )^(^a)</td>
<td>2.78</td>
<td>3.3</td>
<td>4.08</td>
</tr>
<tr>
<td>Dipole moment (Debye) (^b)</td>
<td>3.994</td>
<td>7.209</td>
<td>2.438</td>
</tr>
<tr>
<td>Molar volume (cm(^3).mole(^{-1})) (^c)</td>
<td>260</td>
<td>302</td>
<td>373</td>
</tr>
<tr>
<td>Diffusion coefficient (25°C) ((10^{-10} m^2.s^{-1})) (^d)</td>
<td>6.00</td>
<td>5.49</td>
<td>4.83</td>
</tr>
<tr>
<td>Stokes radius (nm)(^f)</td>
<td>0.41</td>
<td>0.45</td>
<td>0.51</td>
</tr>
</tbody>
</table>

\(^a\) Source: FOOTPRINT Pesticide database, 2009.
\(^b\) Calculated using HyperChem\(^{TM}\) Release 8 software.
\(^c\) Calculated from the group contributions of structural contributions to molar volumes.
\(^d\) Calculated using Eq. (3-4)
\(^e\) Calculated using Eq. (3-5)

Among the three compounds, fenobucarb is the smallest molecule due to its lower \(M_w\). Although having similar \(M_w\), isoprothiolane has a Stokes radius significantly inferior to that of pretilachlor and a higher diffusivity.

In order to facilitate the analytical procedures and to obtain a better accuracy of the measurements, the pesticide concentrations used in this study were about two orders of magnitude higher than those of their relative concentrations found in surface waters in the Mekong Delta (about 10µg/L). It was assumed that this should not have a strong influence, as it has been reported that concentration has a negligible effect on NF separation performances [117]. It should be pointed out that the co-solvent effect (acetonitrile) was not considered since its final concentration was about 1.10\(^{-5}\) mol/L.
3.3.2 Adsorption of pesticides on NF membrane

The sorption experiments were performed in order to assess the adsorption of pesticides due to only solute-membrane surface contact in batch experiments without pressure. This adsorption was mainly affected by the properties of pesticides and by the membrane active layer material.

3.3.2.1 Adsorption kinetics

The variation of the amount of the pesticides adsorbed from single solutions with contact time on the NF270 and NF90 membranes is shown in Figure 3-1(a) and Figure 3-1(b), respectively.

![Figure 3-1: Adsorption kinetics of the three studied pesticides on NF270 (a) and NF90 (b).](image)

It was found that the rate of pesticide uptake on the two NF membranes was somewhat slow. As can be seen in, Figure 3-1(a), a plateau is reached only after 24 hours of contact with the NF270 membrane in the case of fenobucarb and isoprothiolane, while it takes about 4 hours for pretilachlor. On the other hand, the same trend is observed in Figure 3-1(b) for adsorption on NF90. The rate of uptake, however, appears to be slower in the case of pretilachlor with a plateau reached only after 48h of equilibrium. This contact time was chosen for the rest of the study.

3.3.2.2 Amount of pesticide adsorbed

The amount of pesticide adsorbed on the NF270 and NF90 membranes from single and mixed solutions after a contact time of 48 h is reported in Figure 3-2.
Figure 3-2: Adsorbed amount of pesticides on NF membranes from single solute system and from mixtures (Fen: fenobucarb; Iso: isoprothiolane; Pre: pretilachlor)

It can be seen that the adsorption on both membranes in the single solution as well as in the mixtures was, in general, quite different for the three pesticides. The adsorption of pretilachlor was the highest, followed by isoprothiolane and fenobucarb. This was attributed to hydrophobicity of the three pesticides, pretilachlor being more hydrophobic than isoprothiolane and fenobucarb with $\log K_{ow}$ 4.08, 3.3 and 2.78, respectively.

In the single pesticide system, the adsorption of fenobucarb and pretilachlor on the NF90 membrane was slightly higher than that of NF270. This is probably due to the fact that NF90 is more hydrophobic than NF270. However, it was reversed in the case of isoprothiolane. This difference will be developed in the next section.

The situation is not so straightforward in the case of the mixtures. The adsorption of the pesticides on NF270 was increased in comparison to that in the single system, except for isoprothiolane. This trend cannot be clearly explained by the competition between the three pesticides for the adsorption sites. Actually, in the case of competitive adsorption, if the adsorbed amount of the large and more hydrophobic compound, pretilachlor, is expected to increase, that of the other ones should decrease. Moreover, the reverse is observed in the case of NF90, where the adsorption of all the studied pesticides decreased.
3.3.2.3 Absorption isotherm

In this section, the influence of the concentration of pesticides on the amount adsorbed after 48h of contact is presented. Figure 3-3 shows the adsorption isotherms obtained for the three pesticides and the two membranes.

![Figure 3-3: Plot of the pesticides loading on the membrane against the pesticide equilibrium concentration in the liquid phase.](image)

It can be seen that the adsorbed amount in all cases steadily increased with increasing of the equilibrium concentration without reaching a plateau in the studied range of concentration.

To determine the mechanistic parameters associated with pesticide adsorption, experimental data were analyzed according to the well-known models of Langmuir and Freundlich. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It assumes a monolayer adsorption. The Langmuir equation is applied to the adsorption equilibrium as follows:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_mK} + \frac{C_e}{Q_m}
\]

(3-6)

where \(Q_e\) is the amount adsorbed (µg/cm²); \(C_e\) is the equilibrium concentration of the pesticide (µg/L); \(Q_m\) and \(K\) are Langmuir constants related to the maximum adsorption capacity and the free energy of adsorption, respectively. These constants can be obtained when \(C_e/Q_e\) is plotted against \(C_e\).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The logarithmic form of Freundlich model is given by:
\[ \log Q_e = \log K_f + \left( \frac{1}{n} \right) \log C_e \]  

(3-7)

where \( K_f \) and \( n \) are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. These constants can be obtained when \( \log Q_e \) is plotted against \( \log C_e \).

The values of the constants and correlation coefficients from the two isotherms for adsorption of pesticides on the two membranes were reported in Table 3-5.

**Table 3-5: Comparison of Langmuir and Freundlich adsorption isotherm models**

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Freundlich isotherm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fen⁺-NF270</td>
<td>K(_f) (µg.cm(^{-2}))</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td></td>
</tr>
<tr>
<td>Fen-NF90</td>
<td></td>
<td>6.7</td>
</tr>
<tr>
<td>Iso⁺-NF270</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Iso-NF90</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>Pre⁺-NF270</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Pre-NF90</td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td><strong>Langmuir isotherm</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fen-NF270</td>
<td>Q(_m) (µg.cm(^{-2}))</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>k (L.µg(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Fen-NF90</td>
<td></td>
<td>-1.5</td>
</tr>
<tr>
<td>Iso-NF270</td>
<td></td>
<td>9.2</td>
</tr>
<tr>
<td>Iso-NF90</td>
<td></td>
<td>5.6</td>
</tr>
<tr>
<td>Pre-NF270</td>
<td></td>
<td>19.3</td>
</tr>
<tr>
<td>Pre-NF90</td>
<td></td>
<td>11.9</td>
</tr>
</tbody>
</table>

(*) Fen, Iso and Pre designate systems which fenobucarb, isoprothiolane and pretilachlor, respectively, were adsorbed on the NF270 or NF90 membrane. In bold the best fits.

The agreement with the Freundlich model in the concentration range used is good to excellent in all the cases studied (Table 3-5). The experimental data fitting was always better than with the Langmuir model, except for the adsorption of isoprothiolane on NF90 where the coefficients of determination \( R^2 \) are very close. It should be noted that linear plots of \( C_e/Q_e \) versus \( C_e \) are obtained for isoprothiolane and pretilachlor on the NF90 membrane and pretilachlor on the NF270 membrane, indicating that the adsorption of these pesticides on the given NF membranes might follow the Langmuir model. Nevertheless, it was assumed that the adsorption of pesticides
on NF270 and NF90 obeys the Freundlich isotherm model because of the very good agreement obtained in any cases.

In addition, the shape of isotherm curves (slope at the origin) in Figure 3-3 emphasizes the affinity between pesticides and membranes. For instance, the low affinity of fenobucarb for the NF270 and NF90 surfaces can be seen both from the similarly low adsorbed amount and the shallow slope at the origin in the adsorption isotherm. The weak interaction of this pesticide with the studied membranes likely comes from its low hydrophobic character. Moreover, it can be noted that no clear difference was noticed between the two membranes despite the higher hydrophobicity of NF90 compared to NF270. Inversely, a sharper slope at origin can be observed for pretilachlor indicating its high affinity for the membrane surfaces. In this case, NF90 exhibited the larger value as expected.

Interestingly, the slope at origin of isoprothiolane on NF270 was higher than that on NF90 notwithstanding its lower hydrophobicity. This difference, which was also observed in the previous section, might be explained by the high dipole moment of isoprothiolane (7.2 Debye). The molecular structure with a partial positive charge in the dithiolane moieties can help isoprothiolane to interact with a high negatively charged membrane, like NF270, better than another (Table 3-1). A similar effect due to solute polarity was observed by Plakas et al. [111]. They observed a higher amount of isoproturon adsorbed on the negatively charged membrane NF270 in a comparison to the less charged membrane XLE, although the hydrophobicity of XLE was higher than that of NF270.

Moreover, the correlation shown in Figure 3-4 between the adsorbed quantity and the octanol-water partition coefficient that is representative of the hydrophobicity (log $k_{ow}$) can bring deeper insight into the hydrophobicity effect on the adsorption. It should be noted that the value of the pretilachlor adsorbed amount in Figure 3-4 was divided by 3.3 due to its initial concentration about three times higher than the others. The experimentally adsorbed amount fits well in most cases with a linear regression. It can be inferred that the adsorption in these cases is mainly affected by the pesticide hydrophobicity. It is observed that the excellent agreement (coefficient of determination close or equal to one) for the mixed solutions (systems 3 and 4) indicating that adsorption is additive and not competitive. By contrast, the non-linearity of the function in the case of the single solution for NF270 arises from the high adsorption of isoprothiolane (system 1).
Finally, it can be observed in Figure 3-3, that the amount of pesticide adsorbed at low concentration was quite low, less than $0.34 \mu g/cm^2$ for fenobucarb and isoprothiolane at 30 $\mu g/L$ and $1.71 \mu g/cm^2$ for pretilachlor at 100 $\mu g/L$.

It can be then concluded that adsorption on the surface of the NF90 and NF270 membranes can be negligible in real conditions of pesticide concentration in surface waters in the Mekong Delta. The question to be addressed is: can the adsorption, even if low, affect the expected performance of the studied NF membranes?

3.3.3 Rejection of pesticides in pure water solution

3.3.3.1 Rejection of single solution

The rejection of fenobucarb ($M_w = 207.3$), isoprothiolane ($M_w = 290.4$) and pretilachlor ($M_w = 311.8$) by the NF270 and NF90 membranes at an applied pressure of 11 bar is depicted in Figure 3-5. Generally, the rejection by NF90 was higher than by NF270. A similar rejection for all of pesticides used was observed in case of the NF90 membrane with values higher than 95%.

This experimental data can be explained as a first approximation by the membrane MWCO (Table 3-1). In the case of NF90, it is smaller (200 Da) than $M_w$ of all the pesticides, while NF270 is a membrane with larger pores with a MWCO (300 Da) similar to $M_w$ of the larger pesticide.
In fact, as the pesticide molecules are neutral solutes, it is then expected that the rejection by the NF membranes is predominantly governed by the size exclusion mechanism. So, for NF270, an enhancement of the rejection (from 70% for fenobucarb to 94% for pretilachlor) was observed by increasing the Stokes radius of pesticides (Table 3-4). These results confirm the sieving mechanism in which, pretilachlor, the pesticide with the largest Stokes radius displayed the greatest rejection, followed by isoprothiolane and fenobucarb.

It can be noted that the rejection of isoprothiolane was much lower than that of pretilachlor although their $M_w$ are quite similar. However, its stoke radius (0.45 nm) and its high dipole moment ($\mu_0 = 7.21$ Debye) provide a good explanation for this contrast. Despite their close $M_w$, isoprothiolane has a Stokes radius much lower than that of pretilachlor. On the other hand, components with a high dipole moment are less efficiently removed because the dipoles are directed perpendicularly to the membrane and permeate more easily. This was mentioned by many authors [110][117][118][119][120]. It can then be concluded that the rejection of the studied pesticide by relatively wide pore-size NF membranes can be influenced not only by the sieving parameters but also by physicochemical interactions taking place between these organic molecules and the membrane surfaces, as already reported for other molecules [44].
3.3.3.2 Effect of trans-membrane pressure

As mentioned in the previous chapter, the applied pressure can affect the rejection since convection becomes dominant over diffusion by increasing the permeate flux. In the case of the sieving mechanism without any other interactions, the limiting rejection depends only on the solute size to pore size ratio. It is crucial to know how rejection varies with trans-membrane pressure to get a better understanding of the mechanism of pesticide NF. The rejection results of the three pesticides at different trans-membrane pressure are presented in Figure 3-6.

![Figure 3-6: Pesticide rejection at different pressures applied in the case of (a) NF270 and (b) NF90 membranes.](image)

In summary, the trans-membrane pressure seemed to have only a slight effect on the rejection of pesticides. This is especially true for NF90, which rejected at more than 95% the three pesticides, indicating that the experimental limiting rejection was reached in the range of studied pressures. This result was expected because the solute size to pore size ratio is close to unity for all the pesticides. By contrast, the rejection of fenobucarb by NF270 steadily increased from about 63 to 70% for pressures going from 5 to 11 bar meaning that the experimental limiting rejection was not reached in that case. Using higher operating pressure with NF270 could lead to a better removal of the smaller pesticide.

It should be noted that the small decrease observed for pretilachlor and isoprothiolane rejection for applied pressure above 5 bar likely comes from the formation of a concentration polarization layer related to the high flux of the NF270 membrane (about 150 and 180 L.h⁻¹.m⁻² at 11 bar, respectively).
In addition, the function between the permeate flux of pesticide solutions and applied pressure through these membranes is shown in Figure 3-7. Generally, the permeate flux through NF270 was higher than through NF90. This observation can be explained by the property of these membranes discussed in section 3.2.1., i.e., NF270 is less compact with looser pores than NF90.

For NF270, the sequence of the permeate flux was $J_{\text{fenobucarb}} > J_{\text{isoprothiolane}} > J_{\text{pretilachlor}}$. This result was attributed to the concentration polarization resistance. Since owning a high diffusion (Table 3-4), the accumulation of fenobucarb near the membrane surface is lower than that of other pesticides. As results, its concentration polarization resistance is lowest, as well as the flux of this solution is highest and followed by those of isoprothiolane and pretilachlor.

On the other hand, the fluxes of these solutions were almost similar in case of NF90. Because of its small pore size, the effect of the pore-blocking resistance is dominant, instead of the resistance of the polarization layer. Besides, as mentioned above, the solute size to pore size ratio for these pesticides is similar.

### 3.3.3.3 Effect of coexisting pesticides

The real waters in the Mekong Delta consist of a very complex matrix containing, among others, salts and a cocktail of pesticides, as explained in Chapter 1. The following two sections will be devoted to the study of the influence of coexisting species on the pesticide rejection. The effect of coexisting pesticides on the rejection performance of the NF270 and NF90 membranes was evaluated by comparing the removal efficiency in the cases of single pesticide solutions and
of mixed solutions containing the three pesticides. The experimental results are shown in Figure 3-8 for filtration done at 11 bar.

![Figure 3-8: Rejection of pesticides from single solution and mixed solutions at a pressure 11 bar by (a) NF270 and (b) NF90 membrane (the number upper columns is the permeate flux (L/m²h))](image)

For the NF270 membrane, influence of coexisting pesticides was different depending on the size of solutes (Figure 3-8 (a)). The fenobucarb rejection obtained for the mixtures experiment was considerably higher than that of the single pesticide experiment, while those of isoprothiolane and pretilachlor were similar (within experimental error) in the two kinds of experiments. It was demonstrated in section 3.3.2 that competitive absorption (static experiment) on a membrane surface can be considered to be negligible. Since pretilachlor and isoprothiolane are highly retained, they can form a dynamic layer at the membrane surface causing a hindrance effect to the fenobucarb permeation.

In the case of the NF90 membrane, the rejection appears not to be influenced by the presence of the other pesticides. This observation can be explained by the fact that the removal efficiencies of the three pesticides were similar for NF90.

### 3.3.4 Rejection of pesticides in synthetic representative river water

Synthetic solutions were prepared by mixing the three pesticides with a mixture of four salts (NaCl, Na₂SO₄, CaCl₂ and MgCl₂) in proportions and concentrations representative of surface waters occurring in the Mekong Delta (see section 1.1.5.7). The higher concentration of salts is observed during the dry season and depends on the location within the Mekong Delta. Two salinity values were studied approximately corresponding to the median and the highest concentration measured in 2012 with TDS of about 6000 and 26000 ppm, respectively. Filtration
experiments were carried out with the two synthetic river water matrices at 11 bar. The purpose of these experiments was to evaluate the effect of the occurrence of salts in the Mekong river water on the rejection of the studied pesticides. The rejection of fenobucarb, isoprothiolane and pretilachlor compared to that in pure water is shown in Figure 3-9.

Figure 3-9: Pesticides rejection by (a) NF270 and (b) NF90 membrane (no salt, from pure water without salt; Med, from the synthetic water with the median concentration value of salts; Max, from the synthetic water with the maximum concentration value of salts; the number upper columns is the permeate flux (L/m$^2$h))

When comparing the different matrices, it is observed that the rejections with pure water were generally higher than those with synthetic river waters, for all pesticides and membranes used. Similar behavior has been also observed by Zhang et al. [113] (an enhanced passage of bisphenol A through the Desal 5 DK membrane by increasing the NaCl concentration), and by Plakas et al. [111], who studied the herbicide removal in presence of NaCl and CaCl$_2$. Some hypotheses were proposed to account for these reductions, including pore swelling, decrease of solute hydrodynamic radius (Stokes radius), or a combination of the two.

Adding a salt in the feed solution leads to an increase in counter-ion concentration in the electrical double-layer at the surface of the pores and consequently to a greater compaction of the electrical double-layer resulting in an apparent widening of the pore size (so-called pore swelling). On the other hand, when the presence of salts increases, water solvates the salts in preference to the pesticide molecules by a salting out effect. So the hydrated radius of pesticides might be less than the Stokes radius determined in the absence of salt (Table 3-6). Hence, they could permeate more freely through the membrane. However, it is commonly believed that the
swelling of pore size was negligible for ionic strengths less than 100 mM, because it was previously observed that the pure water permeability was constant [113] or decreased [111] after membrane operation.

In this study a strong rejection reduction was observed for NF270 whereas it was limited with NF90. On the other hand, an increase in water flux after each membrane operation is also observed. As seen in Table 3-6, the reduction of pure water flux ($\text{FR}_{\text{PW}}$ (%) calculated from equation (3-3) exhibits a negative value indicating a pure water flux increase of about 10 %. This phenomenon can then be related to the pore swelling effect in presence of high concentration of salts. No clear differences can be seen between the two salinity values, especially in the case of NF90.

Table 3-6: Ion rejection (%) results in the absence and presence of pesticides and pure water flux increase after each experiment

<table>
<thead>
<tr>
<th></th>
<th>NF270</th>
<th>NF90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>max conc. ‡</td>
<td>med conc. ‡</td>
</tr>
<tr>
<td></td>
<td>A †</td>
<td>P †</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>17.2</td>
<td>20.1</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>69.1</td>
<td>75.8</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>48.8</td>
<td>57.4</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>24.3</td>
<td>28.5</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>90.8</td>
<td>91.5</td>
</tr>
<tr>
<td>Cond. (mS)</td>
<td>26.7</td>
<td>26.7</td>
</tr>
<tr>
<td>$J_{\text{wb}}$ (Lh(^{-1})m(^{-2}))</td>
<td>85.3</td>
<td>83.6</td>
</tr>
<tr>
<td>$\text{FR}_{\text{PW}}$(%)</td>
<td>-14.2</td>
<td>-12.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>NF270</th>
<th>NF90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>max conc.</td>
<td>med conc.</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>P</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>59.1</td>
<td>60.0</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>98.3</td>
<td>98.2</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>94.4</td>
<td>96.5</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>66.6</td>
<td>67.3</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>98.8</td>
<td>98.7</td>
</tr>
<tr>
<td>Cond. (mS)</td>
<td>63.8</td>
<td>64.3</td>
</tr>
<tr>
<td>$J_{\text{wb}}$ (Lh(^{-1})m(^{-2}))</td>
<td>7.9</td>
<td>6.6</td>
</tr>
<tr>
<td>$\text{FR}_{\text{PW}}$(%)</td>
<td>-5.8</td>
<td>-9.7</td>
</tr>
</tbody>
</table>

* A and P designate solution with the absence or the presence of pesticides, respectively.
** $J_{\text{wb}}$ is the initial pure water flux
‡ Max conc. and med conc. designate the feed synthetic river waters with the maximum concentration and median concentration values of salts

Finally, ion rejection data in absence and presence of pesticides are summarized in Table 3-6. As seen, even if some discrepancies can be noticed in the case of NF270 for the solution at the maximum salinity, the presence of pesticides does not overall exert any significant impact. On the other hand, the rejection of monovalent ions tended to decrease when their concentration in the feed solution increased for all membranes used.
At this point, modeling the pesticide rejection by using the Nanoflux® software could help us to better understand the mechanism of rejection and bring insight into the feasibility of reliably predicting NF membrane performance.

3.3.5 **Modeling the pesticide rejection by using the Nanoflux® software**

The rejection simulation by using the Nanoflux® software for the three pesticides in the single and mixture solution and in mixed solution with different salt concentration in case of the NF270 and NF90 membranes was carried out. The modeling was calculated by using different adjusting modes of input parameters, including $R_p$ and $R_p+L_{eff}$ adjustment to compare with the calculation done without adjustment. The effective membrane pore size from the Nanoflux® database (0.535 and 0.42 nm for NF270 and NF90, respectively) was used for the calculation in case of no adjustment. The results of modeling are shown in the appendix and summarized in Table 3-7. According to the residual standard deviations between experimental and calculated values, it is observed that the $R_p+L_{eff}$ adjustment mode give the best fitting between experimental and calculated values in all studied cases.

**Single pesticide solution** – According to the residual standard deviations (RSD) between experimental and calculated values, it can be seen that the $R_p+L_{eff}$ adjustment mode give the best fitting between experimental and calculated values for both membranes. In the case of NF270, the experimental data do not fit well with the predicted values when using the $R_p$ value of 0.535 nm determined from the rejection of a homologous series of ethylene glycol oligomers. The effective pore size value is firstly trying to fit in order to get a single parameter global picture of the system behavior. As seen in Table 3-7, much better fitting were then obtained by increasing the pore size value to 0.65 nm. The fitting can be even refined by adjustment of $L_{eff}$. The same trend was observed with the NF90 membrane. In that case, calculation could not be done by the software with the database $R_p$ likely because of the high rejection for these solutes. The best fit was obtained by increasing $R_p$ of about 25 % to 0.52 nm.

**Mixed pesticide solution** – The mixtures contains a total concentration of pesticides higher than their single solution. To obtain the best fitting, the apparent $R_p$ has to be decreased at an intermediate value (0.616 nm) between that previously determined for the single solutions (0.650 nm) and that of the database (0.535 nm) in the case of rejection experiments carried with NF270. It should be mentioned that no influence could be detected with NF90.
Table 3-7: The summary result of the pesticide rejection modeling by the Nanoflux® software

<table>
<thead>
<tr>
<th>Solution</th>
<th>Adjusting mode</th>
<th>NF270</th>
<th>NF90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R_p$</td>
<td>$R_{SD}$</td>
</tr>
<tr>
<td>Single pesticide</td>
<td>No</td>
<td>0.535</td>
<td>0.0553</td>
</tr>
<tr>
<td></td>
<td>$R_p$</td>
<td>0.679</td>
<td>0.0114</td>
</tr>
<tr>
<td></td>
<td>$R_p + L_{eff}$</td>
<td>0.650</td>
<td>0.0052</td>
</tr>
<tr>
<td>Mixed pesticides without salts</td>
<td>No</td>
<td>0.535</td>
<td>0.0249</td>
</tr>
<tr>
<td></td>
<td>$R_p$</td>
<td>0.633</td>
<td>0.0073</td>
</tr>
<tr>
<td></td>
<td>$R_p + L_{eff}$</td>
<td>0.616</td>
<td>0.0053</td>
</tr>
<tr>
<td>Mixed pesticide + Salts at $C_{med}$</td>
<td>No</td>
<td>0.535</td>
<td>0.0682</td>
</tr>
<tr>
<td></td>
<td>$R_p$</td>
<td>0.693</td>
<td>0.0250</td>
</tr>
<tr>
<td></td>
<td>$R_p + L_{eff}$</td>
<td>0.758</td>
<td>0.0094</td>
</tr>
<tr>
<td>Mixed pesticide + Salts at $C_{max}$</td>
<td>No</td>
<td>0.535</td>
<td>0.0717</td>
</tr>
<tr>
<td></td>
<td>$R_p$</td>
<td>0.662</td>
<td>0.0327</td>
</tr>
<tr>
<td></td>
<td>$R_p + L_{eff}$</td>
<td>0.800</td>
<td>0.0120</td>
</tr>
</tbody>
</table>

Mixed pesticide solution – The mixtures contains a total concentration of pesticides higher than their single solution. To obtain the best fitting, the apparent $R_p$ has to be decreased at an intermediate value (0.616 nm) between that previously determined for the single solutions (0.650 nm) and that of the database (0.535 nm) in the case of rejection experiments carried with NF270. It should be mentioned that no influence could be detected with NF90.

Mixed pesticide solution in the presence of salts – Prediction of rejection data obtained with NF270 when experiments were performed in salted solutions requires increasing the $R_p$ values. The more the salt concentration, the higher the apparent pore size must be expanded. Again, the value of 0.52 nm appears to be the best for NF90.

Actually, the real pore size change obtained from the Nanoflux® modeling to get the best fitting seems illogical in the sight of physics, but it shows that the variations arise from other interactions that the effective pore size reflects. These supplementary solute-membrane interactions are not easy to apprehend and therefore they are introduced into a phenomenological coefficient, $k^{res}$ (as mentioned in section 1.2.3.3.3).

In the case of without salts, the dipole – membrane interaction plays an important role, the solute with high dipole moment may give a less rejection than other at similar Stoke radius (as
Chapter 3  II  Removal of pesticides used in the Mekong Delta by nanofiltration

discussed in previous part) [117]. For instance, the studied pesticides are relatively large in comparison with the pore size determined from the ethylene glycol oligomers \(0.7 < r_s/r_p < 0.95\) for NF270 and \(>1\) for NF90). Thus, the theoretical rejection calculated by the hindered transport model for neutral solutes is higher than 90\% for these three pesticides. However, the experimental rejection is lower than that value, due to the dipole-membrane interaction. Hence, to fit with the experiment, the pore size is shifted to higher by the \(R_p\) adjustment or \(R_p+L_{eff}\) adjustment mode. It should be reminded that the modeling results shown in Table 3-7 are calculated with \(k_{res}=1\), means that the other interactions than steric exclusion are negligible.

In the presence of salts, the change of the pore size is more reliable. The supplementary interactions are the screening of attractive dipole-membrane interaction by the salt or the electrostatic ion-membrane. It was reported that the presence of salts in solution can cause an increase in the membrane charge density and hence counter-ions concentration increases in the electrical double-layer at the pore surface. As a result, pore swelling can appear, due to the stronger repulsion forces between the pore walls, especially with elastic polymer membranes as assumed by other authors [121], [122]. The modeling results reflect this point again without taking into account additional interactions than steric exclusion. Therefore, the increase in pore size showed by the modeling is most likely an apparent increase. Nevertheless, this experimental data in agreement with the previous reports confirm that the pesticide rejection decreases in the presence of salts by an apparent pore size augmentation.

3.4 Conclusion

Surface water in the Mekong Delta is a main source for drinking water. The pesticide pollution threatened the source as well as human health. This study showed that NF process was a potential solution to remove pesticides in surface water. The NF90 membrane showed as a crucial choice for removing pesticide when its performance was better than that of the NF270 membrane. The very high rejection by the tight NF90 membrane induced the influence of pressure applied, coexisting pesticide and adsorption of pesticide on membrane performance becoming negligible.

In the single pesticide solution, the rejection of pesticides increased in a corresponding trend with increasing of molecular weight of pesticides. Among the three pesticides, pretilachlor displayed the greatest rejection, because of its greatest molecular size, followed by isoprothiolane and fenobucarb. However, the high dipole moment of isoprothiolane induced its adsorption on the high negatively charged membrane NF270 to increase in a comparison with that on the NF90
membrane. Therefore its rejection by the NF270 membrane was somewhat lower than that expected from its molecular size.

The absorption of pesticides influenced the percentage of pesticides removal, especially in the mixtures. For pretilachlor, the rejection by the NF270 membrane from the mixtures was smaller than that from the single pesticide solution because of the increases absorption amount in the mixture case. Likewise, the rejection of isoprothiolane somewhat increased from the mixtures when its absorption amount decreased. In addition, the results of adsorption experiments showed that the adsorption got equivalent after 48h, the amount of pesticide adsorbed increased in a corresponding with increasing of hydrophobicity of pesticides in a single pesticide solution and also in mixtures. The comparison between adsorption isotherms was shown that Freundlich isotherm was more fixed than Langmuir isotherm and they were physico adsorption.

In the presence of salts, the rejection tended to reduce for all pesticides and membranes used, while the rejection of salts seemed to be independent on the presence of pesticides. Especially, there was an increase of pure water flux after each experiment with the presence of salts in both cases of the two membranes. This showed that both the swelling of pores and the decrease of pesticide Stokes radius sound parameters to be considered for the reduction in rejection of the pesticides when salt concentration increases.

In addition, the increase of the trans-membrane pressure posed no effect on the pesticide rejection. The hindrance effect of the big molecular from the mixtures also affected the rejection of small one.

Modeling the pesticide rejection by using the Nanoflux® software shows that some supplementary solute-membrane and solute-solute interactions which can be reflected by the apparent change of the effective pore size impact the pesticide rejection performance of NF membrane. These results once again confirm the pesticide rejection decreases in the presence of salts that can be evidenced by a by the pore swelling.
Chapter 4

Desalination by electrodialysis
Chapter 4
Desalination by electrodialysis

4 Desalination by electrodialysis

4.1 Introduction

According to estimation of the WHO that by 2025, the world-wide demand for fresh water will exceed supply by 56% [123]. To respond this needs, sea and brackish water become a promising source because more than 97% of all our planet’s water is salty ocean water. However, unlike other sources of clean water as rain water, surface water, and ground water, the salty water treatment for drinking water is faced with major challenges, especially on the issue of energy consumption.

Desalination is a term used to describe the process, involving in the removal of dissolved mineral salts, organic substances, bacteria and viruses, and solids from seawater to obtain freshwater. The major function of the process is to remove essentially salt content or salinity of water [43]. The desalination technology has investigated and developed since 1960s. Recently, many of them can be applied in industry as well as meet the strict requirements of water quality and product price.

Desalination technology includes two main processes: distillation and membrane separation. The distillation processes, such as the multistage flash (MSF) distillation, the multi-effect distillation (MED), and vapor compression (VC) involve phase changes by using thermal energy and mechanical energy. Two common membrane processes are reverse osmosis (RO) and electrodialysis (ED). There is no phase change but the mechanical or electric energy is used to separate substances by semipermeable membranes.

ED application is still limited (about 3% of 74.8 million m$^3$/d installed desalination capacity over the world in 2011) [123] or only used in a small capacity system. However, this method has many special advantages, such as relatively high water recoveries (50 – 90%) [43], no need an energy conversion step (e.g. electrical to mechanical energy in the high pressure pumps, electrical energy can be directly utilized which makes ED also suitable to combine with renewable energy sources). An ED system can operate over a wide pH range (pH 1.0–13.0) as well as a wide temperature range (up to 43°C) [43].

However, the performance of ED for desalination is affected by some operating conditions, which detail presented in section 1.1.3. Thus, a systematic study on the desalination performance of ED process should be done in order to have a full understanding the transport through ion exchange membrane of electrolytes and to choose the optimal conditions for the design module.
In this chapter, the performance of ED process for removal of NaCl was evaluated by a series of experiments under various feed composition and operating conditions. In addition, in order to investigate the feasibility of coupling with NF of ED, the desalination experiments were carried out with permeate solutions of NF processes, and also with the synthetic model water samples representative of surface water found in the MD directly.

4.2 Materials and methods

4.2.1 Experiment equipment and membranes

An ED setup consists of: a DC generator, a concentrate reservoir, a dilute reservoir, an electrode rinsing reservoir with the volume of 2L, three magnetic drive pumps (Siebec M7, England) installed each with a flow-meter and three valves to control solution flow rate in the compartments of ED cell. A diagram of the ED setup working in recirculation mode is presented in Figure 4-1.

Figure 4-1: Schematic of the batch recirculation mode ED system used in this study

(1) DC generator; (2) ED cell; (3) Electrode rinsing reservoir; (4) Dilute reservoir; (5) Concentrate reservoir; (6) Pump; (7) Valve; (8) Flow-meter
The ED experiments were carried out on a PCCell ED 64-004 cell (PCA GmbH, Heusweiler, Germany). This cell was packed with 7 pieces of anion-exchange membranes and 8 pieces of cation-exchange membranes, spacers and a pair of electrodes (anode and cathode). The active membrane area was 64 cm$^2$. The plastic spacers were placed between the membranes to form the flow paths of the diluate and concentrate streams of which the width was 0.5 mm. Both electrodes are made of Pt/Ir-coated titanium.

PC-SK standard cation exchange membranes and PC-SA standard anion exchange membranes (PCA GmbH, Heusweiler, Germany) were used in the stack. Information about the membranes is given in Table 4-1, which was supported by the manufacturer.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>Ion exchange capacity (meq/g)</th>
<th>Chemical stability (pH)</th>
<th>Permselectivity</th>
<th>Functional groups</th>
<th>Surface resistance (Ω.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-SK</td>
<td>130</td>
<td>≈ 1</td>
<td>0 – 11</td>
<td>&gt; 0.93</td>
<td>–SO$_3^-$</td>
<td>0.75 – 3</td>
</tr>
<tr>
<td>PS-SA</td>
<td>90 – 130</td>
<td>≈ 1.5</td>
<td>0 – 9</td>
<td>&gt; 0.96</td>
<td>–NR$_4^-$</td>
<td>1 – 1.5</td>
</tr>
</tbody>
</table>

### 4.2.2 Electrodialysis experiment

All experiments were carried out in batch recirculation mode. The electrode rinse solution was 0.2 mol/L Na$_2$SO$_4$ with a volume of 1 L. The sulfuric salt was used to prevent generation of chlorine gas. The flow rate of this solution was maintained at 1.0 L/min during all experiments while that of diluate and concentrate solutions was controlled by valves to match the investigated values. The same feed solutions were filled in the diluate and concentrate reservoirs. The solutions in the three reservoirs were circularly pumped to the ED cell 5 min for a stabilization step without applied voltage. Then, the voltage was applied to start the desalination and kept constantly during the experiment. The pH and conductivity of the solutions were recorded in time by the pH and conductivity meter with the electrodes immersed in each reservoir (diluate, concentrate and electrode).

The experiment is stopped when the conductivity of the diluate decreases 90%, i.e., the ratio between conductivity at time $t$ and the initial one of the diluate ($\sigma/\sigma^o$) is about 0.1. After
each experiment, the setup was cleaned repeatedly with DI water until the conductivity of the rinsing solution was similar to that of DI water.

Desalination experiments using ED were carried out to determine the performance of the system with three levels of NaCl concentrations in the feed solution: 0.05, 0.1 and 0.25 mol/L. To study the impact of applied voltages, the desalination process experiments were carried out at 5, 10, 15 and 20 V. The influence of divalent cations on the ED performance were investigated on the desalination of 0.1 mol/L NaCl solution containing Ca$^{2+}$ or Mg$^{2+}$ at concentration of 0.005, 0.01 and 0.05 mol/L. These concentrations were chosen based on the range of them in real river water in the MD. The effect of feed solution flow rate was tested at 0.25, 0.5, 1.0 and 1.5 L/min.

4.2.3 Test solutions

In this chapter, desalination experiments were carried out with the permeate solutions of NF in chapter 3 and the two synthetic river water solutions to investigate the possibility of coupling with NF process. Basing on the salt rejection by NF in section 3.3.4, some permeate solutions which exceeded the guideline for drinking water set by the Ministry of Health of Vietnam (QCVN 01:2008/BYT) were chosen to test by ED process. Their composition is showed in Table 4-2.

Table 4-2: The composition of the permeates in NF processes

<table>
<thead>
<tr>
<th>Permeate</th>
<th>NF feed solution</th>
<th>NF membrane</th>
<th>Na$^+$ a mg/L</th>
<th>Mg$^{2+}$ mg/L</th>
<th>Ca$^{2+}$ mg/L</th>
<th>Cl$^- a$ mg/L</th>
<th>SO$_4^{2-}$ mg/L</th>
<th>Cond. mS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate 1</td>
<td>Max b</td>
<td>NF270</td>
<td>5121</td>
<td>300</td>
<td>136</td>
<td>9083</td>
<td>138</td>
<td>24</td>
</tr>
<tr>
<td>Permeate 2</td>
<td>Max b</td>
<td>NF90</td>
<td>2641</td>
<td>16</td>
<td>16</td>
<td>4220</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Permeate 3</td>
<td>Med c</td>
<td>NF270</td>
<td>986</td>
<td>52</td>
<td>21</td>
<td>1718</td>
<td>43</td>
<td>5</td>
</tr>
<tr>
<td>Permeate 4</td>
<td>Med c</td>
<td>NF90</td>
<td>174</td>
<td>5</td>
<td>5</td>
<td>287</td>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>

a The value in bold are the exceeded guideline values
b The synthetic river water with the maximum concentration value of salts
c The synthetic river water with the median concentration value of salts

According to the Table 3-2, two synthetic river water solutions, the maximum and medium solutions, were prepared for ED experiment.

All of inorganic salts used to prepare these solutions were supplied by Sigma Aldrich (ACS reagent grade).
4.2.4 Analytical methods

The pH was measured by a pH meter (Fisher Bioblock Scientific, France) with integrated temperature sensor.

Conductivity was measured by a conductivity meter (Fisher Bioblock Scientific, France). The current and the total voltage of the ED setup were measured by a multimeter 1705 (AIM – TTi, United Kingdom).

4.2.5 Data evaluation method

For the purpose of studying on the effects of voltage, concentration, flow rate, divalent cations on the ED cell performance, all experiment results firstly focus on the concentration changes in the diluate compartment. The optimal conditions of ED process, as well as their performance were evaluated based on the following parameters:

**Operation time**

The operation time is the time needed to remove 90% of salinity of the diluate compartment (measured via the electrical conductivity).

**Apparent rate constant**

During the desalination process, the differential ion concentration of the diluate compartment in time is proportional to the current as shown:

$$\frac{dc}{dt} = KI$$  \hspace{1cm} (4-1)

At low value, the current is given by Ohm’s Law, as followed:

$$l = \frac{U}{R_{st}}$$  \hspace{1cm} (4-2)

where $U$ is the electric potential difference (V) and constant as a condition mode, $R_{st}$ is the apparent resistance of the total membrane stack ($\Omega$). Assumed that $R_{cc}$, $R_{cm}$, $R_{am}$ and $R_{e}$ are negligible in the in a first approximation, it can be calculated by equation (1-35) as:

$$R_{st} = N R_{dc}$$  \hspace{1cm} (4-3)

The resistance of the diluate compartment ($R_{dc}$) is a function of the ion concentration in the diluate compartment by equation (4-4):

$$R_{dc} = \frac{l}{A_{c}s}$$  \hspace{1cm} (4-4)
where \( C \) is the ion concentration in the diluate compartment (mol/m\(^3\)) and \( \Lambda \) is the molar conductivity of the solution (S m\(^2\)/mol), \( S \) is the area of compartment means area of membrane (m\(^2\)), \( l \) is the width of compartment means the thickness of spacer (m).

Substituting equation (4-2), (4-3) and (4-4) into equation (4-1) and rearranging, it was obtained

\[
\frac{dC}{dt} = \frac{K \Lambda AS}{N t} C
\]  
(4-5)

This equation is similar to the rate equation of first order reaction:

\[
-\frac{d[A]}{dt} = k [A]
\]  
(4-6)

where \( k \) is the first order rate constant, which has units of min\(^{-1}\).

The integrated first order rate law is

\[
\ln[A] = -k t + \ln[A]_0
\]  
(4-7)

where \([A]\) is concentration of ion or conductivity of solution at time \( t \). To determine \( k \), a plot of \( \ln[A] \) vs. time \( t \) gives a straight line with a slope of \(-k\).

The main difference between the different \( k \) comes from the state of the polarization of the cell.

**Energy consumption**

As mentioned in section 1.3.6, energy consumption in electrodialysis includes the electrical energy consumed by the stack and the pumps. In this chapter, only the energy consumed by the stack is considered while assumed that the pump energy consumption changes negligibly in different ED conditions.

The stack energy consumption is proportional with the voltage and current applied to the stack at time \( t \) as equation (1-47).

\[
E_{des} = \int U I dt
\]  
(4-8)

where \( E_{des} \) is the energy consumed in a stack for the transfer of ions (kWh/m\(^3\)). As mentioned above, the ED process was carried out in voltage constant. Thus, equation (4-8) can be written as:

\[
E_{des} = U \int I dt
\]  
(4-9)

Depending on the experiment data of total voltage and current was recorded at time \( t \), the stack energy consumption can be calculated.
4.3 Results and discussion

4.3.1 Factors effect to NaCl removal by electrodialysis

4.3.1.1 Effect of concentration

The ratio of the diluate conductivity at time $t$ and at time $0$ as a function of time is shown in Figure 4-2. The ED experiments were carried out with NaCl solutions at concentrations of 0.05, 0.1 and 0.25 mol/L with applied voltage of 5V and flow rate of 0.5 L/min. Generally, the time which needs to remove 90% of salt increases as the feed concentration goes up. It takes 66, 74 and 99 min for the solutions 0.05, 0.1 and 0.25 mol/L, respectively.

![Figure 4-2: The ratio of the diluate conductivity as a function of time for different feed concentration at 5V](image)

The electric power consumption in ED in Figure 4-3 has a same trend with the time operating, whereas the rate constant inversely. It decreases from 0.035 to 0.022 (1/min) for the constant and the increase of power is from 1.1 to 4.5 (kWh/m$^3$) when the concentration increases in the range investigated. In case of 0.1 mol/L NaCl solution, which has a similar conductivity with the brackish water, the power consumption to treat 1 m$^3$ water reaching the guideline of the drinking water is 2.5 kWh.
In addition, in the cases of the feed concentration of 0.1 and 0.25 mol/L, the conductivity ratio gradually decreases during the experiment (Figure 4-2). However, in the case of 0.05 mol/L NaCl, this ratio rapidly decreased within the initial 30 min. After this point this decrease slowed down. This is attributed to both the concentration polarization in the membrane boundary layer as well as depletion of electron carriers in the diluate. Since the residue concentration of the electrolyte NaCl in this compartment after 30 min operating in this case was lower than that in others, the current was not sufficiently transported across the stack. Thus the desalination process became slower from this point.

4.3.1.2 Effect of applied voltage

The applied cell voltage is an important operating condition in ED as the voltage determines the current in the cell and hence the desalination efficiency as well as energy consumption. The ratio of the diluate conductivity as a function of time for different applied voltage is shown in Figure 4-4. The experiments were carried out with NaCl solution at concentration of 0.05, 0.1, 0.25 mol/L.
Figure 4-4: Effect of the applied voltage on the ED process for different feed concentrations (a) 0.05 mol/L, (b) 0.1 mol/L, (c) 0.25 mol/L
As can be seen in case of a feed concentration of 0.05 mol/L NaCl (Figure 4-4(a)), the time to reach the 90% of salt removal decreases as the applied voltage increases (66, 33, 28 and 25 min at 5, 10, 15, and 20 V, respectively). The same trends are also seen in the experiments with the initial salt concentration of 0.1 and 0.25 mol/L NaCl (74, 33, 25 and 24 min in Figure 4-4(b) and 99, 37, 28 and 26 min in Figure 4-4(c) at the same applied voltage conditions, respectively). This can be simply explained by the ion flux through an ion exchange membrane followed by the Nernst–Planck equation (1-28). The flux of ions from the diluate to the concentrate compartment increases due to the increase of applied voltage (or different potential). As a result, the decrease conductivity of the diluate becomes quicker and time operation is shorter.

In all of the three feed concentration cases, the operation time decreases quickly when the voltage rises up to 15 V. This time do not significantly change at higher 15 V. The rate constant in Figure 4-5 has a same trend. From 15 V, these constants level off to a plateau. It can be explain by the voltage-current relation. When the applied voltage increases, the current increases, followed by Ohm’s Law. This current is used to drive ions through membrane. However, when the current reaches a limit value, the increased voltage will not lead to the increased current. Over that point, the current efficiency, which is the current used for the ion transport, decreases and the electric energy is used for heating the solution or for water dissociation.

![Figure 4-5: The rate constant of the desalination process as a function of applied voltage](image-url)
Besides, there is a decrease of rate constant in case of 0.05 mol/L at 15 V and 20 V in comparison with those of 0.1 and 0.25 mol/L NaCl (Figure 4-5). This observation is caused by the limiting current and it was verified that at a lower feed concentration, the limiting current is more quickly got [4].

On the other hand, it should be noted that the operation time for these three solutions is almost similar for a given voltage applied higher 10V (Figure 4-4). This observation releases that the ion exchange capacity limit of the membranes is not reached at the concentration of 0.25 mol/L. Hence, it was approved that ED can be applied at these concentrations.

Figure 4-6: The energy consumption of the desalination process as a function of applied voltage

However, in consideration of energy consumption (Figure 4-6), the increase of required energy in the cases of 0.05 and 0.1 mol/L are similar in the increase of applier voltage (similar slope of linear regression), while the slope in case of 0.25 mol/L is sharper, i.e., the energy consumption increases more quickly. This releases that the current efficiency in this case is lower than that of other feed concentrations, because a part of the electric energy transfers to thermal energy. Since the higher ion density in solution of 0.25 mol/L leads to increasing of ion collisions and releasing the thermal energy.

4.3.1.3 Effect of divalent cations

It is known that the presence of divalent cation may affect the operation time of ED process, due to its lower mobility. Moreover, another challenge of divalent cation presence is
their undesired precipitates at a suitable condition. These precipitates will form a fouling layer at
the phase interface and reduce the performance of the ED process. The effect of divalent cations
was evaluated by comparing the operation time, rate constant as well as energy consumption in
the cases of single NaCl solution (0.1 mol/L) and the presence of Ca$^{2+}$ or Mg$^{2+}$ with different
concentration in that. The ratio of the diluate conductivity as a function of time for different
composition of feed solutions is shown in Figure 4-7. These experiments were carried out at an
applied voltage of 15 V and flow rate of 0.5 mL/min.

![Figure 4-7: The ratio of the diluate conductivity as a function of time for different concentration
of (a) Ca$^{2+}$ and (b) Mg$^{2+}$ in 0.1 mol/L NaCl solution](image-url)
In general, the influence of divalent cations on the operation time increases when their concentration in 0.1 mol/L NaCl solution increases. This is expected because divalent ion diffusivity is higher than that of monovalent ion (Table 2-1). For the Mg$^{2+}$ cation, the time increases from 25 to 33 min when the Mg$^{2+}$ concentration goes up. The effect of addition Mg$^{2+}$ by 0.005 mol/L is negligible with a similar time, 25 min (Figure 4-7 (b)). The same result is observed in the cases of Ca$^{2+}$ 0.005 and 0.01 mol/L (Figure 4-7 (a)). In addition, the effect of Ca$^{2+}$ is less than Mg$^{2+}$. The time for Ca$^{2+}$ 0.05 mol/L is 28 min, whereas it takes 33 min for Mg$^{2+}$ at the same added concentration. It can be explained by the diffusivity of Ca$^{2+}$ is higher than that of Mg$^{2+}$ while its stoke radius is smaller. Thus its mobility through the membrane is easier.

These results are confirmed by the rate constant of the desalination process in Figure 4-8. The rate constant of three Ca$^{2+}$ addition case is almost similar to that of 0.1 mol/L NaCl solution (means 0.092 ± 0.002 min$^{-1}$). For the Mg$^{2+}$ addition, the rate constant decreases rapidly when the concentration added increases from 0.005 to 0.05 mol/L (difference about 0.01 min$^{-1}$).

![Figure 4-8: The rate constant of the desalination process in different feed solution composition](image)

It should be noted that no scaling or fouling was observed in all of experiments. It means that the desalination by ED process can be done in the presence of Ca$^{2+}$ or Mg$^{2+}$ at the concentration up to 0.05 mol/L.
4.3.2 Desalination the permeate solution of NF by ED

4.3.2.1 Effect of voltage

The desalination process for the permeate solutions of NF process was carried out at different applied voltages to evaluate capacity application of this method in this kind of water. The conductivity reduction as a function of operation time of the ED process for each NF permeate water is shown in Figure 4-9.
Figure 4-9: Effect of the applied voltage on the ED process for different NF permeate waters: (a) permeate 1, (b) permeate 2 and (c) permeate 3.
It can be observed that the operation time of desalination process becomes shorter at the higher applied voltages in three cases of NF permeates. This trend is similar to the effect of voltage on the NaCl removal in section 4.3.1.2. As discussed above, it is attributed to the increase of ion flux when the applied voltage increases. However, at the applied voltage above 15 V, the operation time levels off to a value of about 24, 21 and 20 min for the NF permeate 1, 2 and 3, respectively. It means that all kinds of NF permeate solutions can be removed 90% of salinity by ED process during 25 min.

In addition, the rate constant increases with increase of the applied voltage and reaches to the maximum value at 15V for three NF permeate solutions (Figure 4-10). Hence, it can be approved that 15 V is the optimal voltage for the desalination process by ED in this case.

4.3.2.2 Effect of flow rate

The effect of the flow rate of the diluate and concentrate solution on the performance in electrodialysis is not apparent and complicated. The increase of flow rate may cause a quicker reduction of conductivity due to the decrease of concentration polarization resistance. On the other hand, this increase may also cause a reduction of operation time due to the decrease of residence time of ions at the membrane interface. Depending on the flow rate value and the ion concentration in the feed solution, the distribution of these two trends is different and the total effect of flow rate on ED performance is positive or negative.
The ratio of the diluate conductivity as a function of time for different flow rate of diluate solution is shown in Figure 4-11.

Figure 4-11: Effect of the flow rate on the ED process at 15 V for different NF permeate waters:

(a) permeate 1, (b) permeate 2 and (c) permeate 3
In general, the operation time is reduced when the flow rate increases from 0.25 L/min to 1.5 L/min in three cases of the NF permeates. For the NF permeate 1 solution (Figure 4-11 (a)), it takes 36, 24, 21 and 20 min to remove 90% of salinity for the flow rate of 0.25, 0.5, 1.0 and 1.5 L/min, respectively. In the same trend, it respectively takes 36, 21, 17 and 14 min for the NF permeate 2 (Figure 4-11 (b)) and 33, 20, 17 and 13 min for the NF permeate 3 (Figure 4-11 (c)) at the same flow rate condition. It can be observed that at a flow rate above 0.5 L/min, the reduction of the operation time is negligible as the flow rate increases. This reduction can be explained by the decrease of the concentration polarization resistance. Since the increase of solution velocity as the flow rate increases leads to the reduction of boundary layer thickness and the concentration polarization. Thus the transport of ions through the membrane becomes easier and that results in the reduction of the operation time.

However, in case of the NF permeate 1, it can be observed that the salinity reduction at a flow rate of 1.0 and 1.5 L/min during first 12 min was lower than that at flow rate 0.5 L/min (Figure 4-11 (a)). It can be explained by the decrease of residence time of ions at the membrane interface at higher flow rate. Thus these ions do not have enough time to transfer through the membrane. This effect is more dominant than the effect of the boundary layer thickness reduction when the feed solution is more concentrate. The same phenomenon was not found in cases of the permeate 2 and 3.

![Figure 4-12: The rate constant of the desalination process as a function of the flow rate](image-url)
On the other hand, the rate constant of three desalination processes of NF permeate solutions increases with increase of the flow rate from 0.25 L/min to 0.5 L/min, and then almost keeps constant when the flow rate still increases (Figure 4-12). Hence, it can be concluded that 0.5 L/min is the optimal flow rate for the desalination process by ED.

In addition, the chart of energy consumption shows that the flow rate of solution does not exert any significant impact on the electric energy consumption of ED process. A similar behavior has been also observed by Kabay et al. [85].

Figure 4-13: The energy consumption of the desalination process as a function of the flow rate

### 4.3.3 Desalination the simulated river water by electrodialysis

The desalination experiments with the two simulated river waters in the MD were carried out by ED process to evaluate the capable application of ED on these samples. The ratio of the diluate conductivity as a function of time is shown in Figure 4-14. The experiments were performed at the applied voltage of 15 V and the flow rate of 0.5 L/min. The result shows that ED process worked well with the median concentration solution. The salinity reduction reaches 90% after 30 min and consuming 5.3 kWh/m$^3$. The rate constant of this process is 0.083 min$^{-1}$ and it is smaller than that of the process with NaCl 0.1 mol which has a similar conductivity. It is attributed to the presence of divalent cations.
Concerning the maximum concentration solution, it takes 43 min to remove 90% of salinity and consumes 24.7 kWh/m$^3$. This operation time is one and half times longer than that of the median concentration solution while its concentration is four times higher than the median. However its energy consumption is about five times higher than that of the median solution.

Moreover, it is noted that no scaling or fouling was observed during the desalination process in all of investigated cases. Thus, with these results, it can be concluded that these kinds of simulated waters can be directly desalted by an ED process.

**4.4 Conclusion**

In this chapter, ED experiments were systematically carried out with single NaCl solution, the simulated river samples and the NF permeate solution in different conditions of concentration, applied voltage and flow rate. The optimal condition and the performance of ED process was evaluated depending on the operation time, the kinetic rate constant and the energy consumption. Besides, the feasibility of application ED for desalination of the investigated solutions was considered. Depending on the obtained results, we can conclude as follows.

The applied cell voltage is on of important operating conditions in ED. It was observed that the salt removal process became quicker when the applied voltage increased in most of investigated cases. The optimal voltage obtained was 15 V, because the limiting current is exceeded and the transport of ions does not increase at the applied voltage above 15 V. The current efficiency decreases when the applied voltage is above 15 V, due to the consumption of
electric energy by the water dissociation. On the other hand, the energy consumption increases when the applied voltage increases. The increase of energy consumption was different in the different cases of feed concentration. The energy consumption increases more quickly for NaCl solution of 0.25 mol/L in comparison with that of 0.05 and 0.1 mol/L. It means that the current efficiency for the more concentrated solution is lower than that of the dilute ones.

In the presence of divalent cations, the time operation of ED process trends to longer. It can be explained by the differences in mobility of the specific counter-ions transport through the membrane. The divalent cations have a larger Stoke radius and smaller diffusivity than monovalent cations. Therefore, they own a higher resistance when migrating through the membrane and result in the increase of operation time. However, there was no precipitate or fouling observed in all of investigated cases. So the ED process can operate smoothly in the presence of Ca\(^{2+}\) or Mg\(^{2+}\) with the concentration up to 0.05 mol/L.

The impact of the flow rate on the operation time has two opposite trends. Firstly, the increase of the flow rate causes the reduction of boundary layer thickness and the concentration polarization, hence the operation time decreases. Reversely, this increase also leads to the decrease of residence time of ions at the membrane, and the operation time increases since these ions do not have enough time to transfer through the membrane. Depending on the flow rate value and concentration of ions, these two effects are dominant or less than in compare with the other. In all cases of study, the operation time of ED process generally reduced when the flow rate increased from 0.25 L/min to 1.5 L/min. Except the case of the NF permeate 1 (high concentration), the salinity reduction at flow rate of 1.0 and 1.5 L/min during first 12 min was lower than that at flow rate 0.5 L/min, since the decrease of residence time effect is dominant.

Concerning the effect of concentration, this was expected that the higher concentration of salts, the longer operation time took. It was demonstrated that the ion exchange capacity limit of the membranes is not reached at the highest concentration of NaCl studied (0.25 mol/L), NF permeate 1 as well as at the maximum concentration simulated river water. Thus ED process can be applied for these kinds of solutions directly without fouling observed.
Chapter 5

Nanofiltration and electrodialysis coupling
5 Nanofiltration and electrodialysis coupling

5.1 Introduction

As described in Chapter 1, the challenge of surface water treatment in the MD is that there is the simultaneous presence of pesticides and high salinity. Therefore it is difficult to be able to use individual methods to treat thoroughly these two items. The results about NF rejection in section 3.3.4 demonstrated that pesticide rejection performance of both types of membrane NF270 and NF90 is reduced when there is the presence of salt, especially at maximum concentration. In contrast, although not affected by the presence of pesticides, the salt rejection achieved is not enough for the permeate compliance with the requirements of surface water standards, even with membrane having low pore size as NF90. By observing results in Table 4-2, up to three out of four permeates do not attain the standard on Na\(^+\) and Cl\(^-\) content.

Similarly, ED removes salt very well but cannot eliminate pesticides, because these substances are neutral compounds and not be transported through the membrane under the electric driven force. Hence this section will focus on the study of the integration of these two methods to treat the surface water polluted by salinity and pesticides. The membrane process efficiency will be evaluated by monitoring both treatment efficiency and energy consumption.

Actually, this integration has been applied in water treatment although there are different purposes. For instance, ED has been proposed to desalinate the retentate stream of a NF unit to increase water recovery as well as eliminate the mineral scaling in NF [74]. Recently, J. Liu et al. [124] has applied an NF–ED integrated membrane process to separate monovalent and bivalent ions and concentrate them from brine to handle the disposition problem of seawater desalination. In addition, a membrane hybrid process of NF and ED is applied to recover water from the alkaline pulp bleaching effluent [125] or to reuse water in the leather industry [126], in which the role of NF is to remove organic compounds and undertake partial desalination while ED can remove the remaining salt to achieve a high quality of water product.

On the other hand, ED can be combined with seawater and brackish reverse osmosis (SWRO and BWRO), as a pre-desalination technique [70], [127]. ED helps reducing the salt concentration to a desired level or adjusting its concentration of the water product. The application of ED in this hybrid process handles the limitations for ED as well as BWRO. The limitation of high osmotic pressure at higher salt concentrations for a single BWRO process is minimized by ED pretreatment. For the limitation of low conductivity at lower salt concentration for a single ED process, BWRO is used when the internal resistance of the ED stack becomes
high after a certain degree of salt removal. This combination could lead to a desalination cost reduction of about 0.15 €/m³ in a comparison with SWRO [127].

5.2 Materials and methods

5.2.1 ED – NF integrated membrane process

Since the rejection in nanofiltration was found to be affected by the presence of salts, especially at high concentration, the hybrid process of NF followed by ED is not enough efficient. In addition, the proficiency of directly applied model samples on ED process was demonstrated in section 4.3.3. Thus, in this section, the ED-NF integrated process (ED followed by NF) was investigated for the two simulated river water samples, maximum and median concentration solutions. The median concentration solution was firstly desalinated by ED stage, and then sent to NF stage with NF270 installed, whereas the maximum solution was connected with NF90 after ED stage. The schematic diagram of the coupled process with these solutions is showed in Figure 5-1. In each stage, the batch mode experiment was carried out.

![Figure 5-1: The schematic diagram of the coupled process with the maximum and median concentration solutions](image-url)
In order to reduce energy consumption for ED process, the ED stage was fixed at 50% reduction of the overall salt concentration (measured via the electrical conductivity) instead of 90% reduction as done in previous experiments. The experimental procedure of each stage was carried out as follows.

5.2.1.1 ED stage

The ED pilot and ion exchange membranes in these experiments are the same as those in section 4.2.1.

One liter of each model solution including pesticide like experiment in section 3.3.4 was filled to the concentrate and diluate tank. The electrode rinsing tank was filled with Na₂SO₄ solution at a concentration of 0.2 mol/L. The flow rate was maintained at 0.5 L/min for the concentrate and the diluate and 1.0 L/min for the electrode rinsing solution during all experiments. The constant voltage mode was used with 15V applied. Before the experiments were started, the solutions in the three tanks were circularly pumped to the ED cell during 24h to make sure that the adsorption of pesticides on ED setup is saturated and does not affect the result. As mentioned above the ED stage was stopped at 50% reduction and the diluate was collected for the NF stage. Each model solution was repeated 2 times to obtain 2 L of the diluate.

The conductivity, pH, water sample in each reservoir, current and total voltage were recorded every 5 min to evaluate the performance and the energy consumption. All presented ions (Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻) in the collected water samples were determined by an ion chromatograph analyzer (ICS-900, Dionex).

The setup was cleaned repeatedly with DI water after each experiment until conductivity of rinsing solution was similar to that of DI water.

5.2.1.2 NF stage

The experiment procedure in NF stage was carried out as shown in section 3.2.6.2 with some specific differences. The NF pilot after conditioning membrane was filled with 2 L of the ED diluate. The median and the maximum ED diluates were tested with NF270 and NF90, respectively. The pressure was applied at 5 bar.

The pesticide concentrations were analyzed by the DI-LC/MS/MS and the ions was determined by the ion chromatograph (ICS-900, Dionex), as presented in section 3.2.4.
5.2.2 Optimizing the NF process

The experimental procedure was carried out as shown in section 3.2.6.2 with the NF90 membrane for the two kinds of feed solutions: maximum and medium concentration synthetic river waters after removed 50% of conductivity by the ED pretreatment (so-called Max50 and Med50). The filtration experiment was carried out in a batch mode where the permeate is extracted until reaching 80% of recovery.

The instant conductivity of the feed and permeate was recorded during the experiment. The volume flux was calculated by collecting permeate every 5 min and this value was used to calculate the recovery. The feed and permeate samples were taken at each 10% of recovery to determine the salt and pesticide concentrations and calculate the rejection for each specie.

Since the osmotic pressure of feed solutions increases as the recovery increases it results in a flux decline. The applied pressure for filtration experiments in this part was calculated by the Nanoflux® software to make sure that the specific flux of NF 90 (as reported by the manufacturer about 41.6 L/m².h – average operating range of permeate flux) can be obtained at 80% of water recovery. Based on results obtained by modeling, the calculated applied pressures for the Max50 and Med50 experiments are 15 and 12 bar, respectively. This estimation (modeling) assumes that the rejection rate of monovalent and divalent ions is 50 and 99% respectively.

5.3 Results and discussion

5.3.1 ED – NF integrated membrane process

5.3.1.1 ED performance

The reduction of conductivity and ion concentration in the diluates as a function of time are shown in Figure 5-2. It is observed that the concentration of ions in the diluate decreased as the desalination time in both cases of feed solutions. This indicates that all ions can be transported through the ion exchange membrane under electric driven force, although their removal kinetic may be different.

Concerning the anion transport, SO\textsubscript{4}\textsuperscript{2-} ions were removed more slowly, compared to the monovalent Cl\textsuperscript{-} ions, especially beyond 5 min. The transport of specific ions through ion exchange membranes mainly depends on the difference in mobility of the specific counter-ions through the membrane. The sulfate ion has a larger Stokes radius and smaller diffusivity than the chloride ion (see Table 2-1). Therefore, it experiences a higher resistance when migrating through the membrane explaining its lower removal rate.
Concerning the cation transport, their removal rate was almost similar in the case of the maximum inlet solution (Figure 5-2 (b)). Inversely, in the medium inlet solution, the Ca$^{2+}$ ion was removed more slowly than Na$^+$ and Mg$^{2+}$ ions (Figure 5-2 (a)). This result is not parallel with the Stokes radii and diffusivities of these ions (Table 2-1), where Ca$^{2+}$ Stokes radius is larger than that of Na$^+$ and smaller than Mg$^{2+}$ and its diffusivity is lower than Na$^+$ and higher than Mg$^{2+}$. The most likely reason might be from experimental errors since the Ca$^{2+}$ concentration is much smaller than that of two other cations (about 0.001 mol/L of Ca$^{2+}$ in comparison with 0.07 of Na$^+$ and 0.01 of Mg$^{2+}$).

Figure 5-2: The reduction of conductivity and ion concentration in (a) the median (b) the maximum ED diluate as a function of time.
5.3.1.2 NF performance

The rejection performance of NF stage in the ED-NF integrated process (ED pretreatment NF) is evaluated based on the comparison with the rejection of NF process only (direct NF) with using the same membrane but at different applied pressure. The results of the rejection comparisons are shown in Figure 5-3 for the median salinity with NF270 and Figure 5-4 for the maximum salinity with NF90.

For the removal of salts, it was observed that the NF270 performance in rejection of Na$^+$ and Ca$^{2+}$ by two processes was quite similar (Figure 5-3). In the case of Cl$^-$ ions, its NF rejection decreased after ED pretreatment in comparison with the direct NF, while those of Mg$^{2+}$ and SO$_4^{2-}$ increased. The decrease of Cl$^-$ ions can be attributed to a pH change of the NF feed solution. During the ED stage, dissociation of water occurs so that the pH of feed solution decreased from neutral pH ($\approx 6$) to pH 4.4. Thus, as discussed in section 2.3.3 (Fig. 2-9), the Cl$^-$ rejection was lower than in the case at neutral pH (direct NF) due to the Donnan effect.

![Figure 5-3: The rejection of ions and pesticides by NF process with NF270 of the median solution in comparison between with or without ED pretreatment stage](image)

In case of the maximum salinity (Figure 5-4), the rejection of divalent ions by both processes (with and without ED pretreatment) with NF90 was similar, whereas of the rejection of monovalent ions increase after the ED pretreatment. This can be explained by the decrease of salinity originated from the ED stage before the feed is sent to the NF stage. As demonstrated in section 2.3.4, the filtration of NaCl is significantly affected by their concentration due to the
reduction of the normalized membrane charge density with increasing feed concentration. Thus, the NaCl rejection increases at a lower concentration. Besides, the Donnan effect in this case seems to be negligible, although there was also a decrease of the pH solution by water dissociation. The steric hindrance effect is more dominant than the Donnan effect in the filtration of a small pore size membrane, as NF90.

Figure 5-4: The rejection of ions and pesticides by NF process with NF90 of the maximum solution in comparison between with or without ED pretreatment stage.

Concerning the pesticide rejection, for both feed solutions, the performance of NF when ED is used as pretreatment is much better than direct NF. This result was expected because the pesticide rejection will be less affected at the lower salinity. The apparent swelling of membrane pore size is negligible at the low salt concentration, as mentioned in section 3.3.4.

5.3.1.3 Water product quality

In this part, the water product quality is evaluated based on the ion concentration of the water products of the two integration processes, which are ED process followed by NF process with NF270 or NF90. The feed solution with the median salinity was applied to the ED-NF270 process and the maximum salinity solution was applied to the ED-NF90 process. The water product quality is compared with VN guideline for the drinking water enacted by the Ministry of Health (MOH), QCVN 01:2008/BYT and shown in Table 5-1.
Table 5-1: Concentration of ions in water product of the two integration processes

<table>
<thead>
<tr>
<th>Solution</th>
<th>Cond. mS/cm</th>
<th>Na(^+) mg/L</th>
<th>Mg(^{2+}) mg/L</th>
<th>Ca(^{2+}) mg/L</th>
<th>Cl(^-) mg/L</th>
<th>SO(_4^{2-}) mg/L</th>
<th>TDS mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>9.0</td>
<td>1525</td>
<td>232</td>
<td>45.4</td>
<td>2859</td>
<td>505</td>
<td>5167</td>
</tr>
<tr>
<td>Product</td>
<td>1.7</td>
<td>336</td>
<td>10.2</td>
<td>3.9</td>
<td>556</td>
<td>5.2</td>
<td>912</td>
</tr>
<tr>
<td>Feed</td>
<td>27</td>
<td>4888</td>
<td>1013</td>
<td>213</td>
<td>9927</td>
<td>1574</td>
<td>17616</td>
</tr>
<tr>
<td>Product</td>
<td>1.1</td>
<td>120</td>
<td>4.0</td>
<td>7.7</td>
<td>233</td>
<td>9.7</td>
<td>374</td>
</tr>
</tbody>
</table>

It can be observed that the quality of water produced from the ED-NF90 process was in compliance with the VN guideline for all parameters. However, the concentration of Na\(^+\) and Cl\(^-\) in the water produced from the ED-NF270 process exceeded the guideline 1.7 and 2.2 times respectively, although its total dissolved solids (TDS) was a bit below this standard.

5.3.2 Comparison between membrane processes

It has been shown previously that the TDS concentration can have a significant effect on pesticide removal in NF. In order to choose the appropriate treatment using both ED and NF, four different process combinations are considered such as NF270 - ED, NF90 - ED, ED - NF270 and ED - NF90. For each combination, process efficiency and energy consumption have been evaluated for two types of simulated river water samples (Median and Maximum salt concentration solution). The performances of these hybrid processes are evaluated by monitoring the rejection rate of each species in solution (ions and pesticides) and their final concentration in the water product. Results are summarized in Table 5-2.

The pesticide rejection is mainly from NF stage given in section 3.3.4 and 5.3.1. Since salt components can be retained by both NF and ED stage, the rejection results presented in Table 5-2 correspond to the total rejection of the two processes. They are calculated from section 3.3.4 and 4.3.2 for the processes of NF-ED, and from section 5.3.1 for the processes of ED-NF.

The energy consumption for each stage is estimated based on the experimental conditions applied. For the NF process, the energy consumption is calculated based on the work of the high pressure pump while it refers to the electrical energy applied to the system for the ED process.
The specific energy consumption (SEC) in NF process is often used to characterize the energy cost of the process and correspond to the energy (from pump) needed to produce one cubic meter of permeate at a desired water recovery and calculated by the following equation:

\[
E_p = \frac{\Delta P}{36 \eta \gamma}
\]  

where \( E_p \) is specific energy consumption of the pump (kWh/m\(^3\)); \( \Delta P \) is the trans-membrane pressure (bar); \( \eta \) is the efficiency of the pump, \( 0.5 \leq \eta \leq 0.8 \), assumed to be 0.8 in this study; \( \gamma \) is the recovery of the process, \( \gamma = V_p/V_f \), with \( V_f \) and \( V_p \) are the volume of the feed and the permeate obtained after a batch experiment (L), 36 is a factor to convert the unit of energy to kilowatt hour per cubic meter. SEC calculations in Table 5-2 are given purely as a guide as the filtration time was fixed at 15 min so that \( \gamma \) values are low and dependent on the salt concentration (due to the osmotic pressure) and the studied membrane (more or less tight pores).

The electric energy consumption in ED was calculated based on the voltage and current recorded during experiments by equation (4-9).
Table 5-2: Rejection performance and energy consumption to treat two simulated river waters by different coupling of NF and ED

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Simulated water</th>
<th>Rejection performance (%)</th>
<th>Ep (kWh/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fen⁺</td>
<td>Iso⁻</td>
</tr>
<tr>
<td>NF270 (11bar) – ED</td>
<td>Median **</td>
<td>73</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>Maximum **</td>
<td>69</td>
<td>70</td>
</tr>
<tr>
<td>NF90 (11bar) – ED</td>
<td>Median **</td>
<td>94</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Maximum **</td>
<td>88</td>
<td>90</td>
</tr>
<tr>
<td>ED - NF270 (4bar)</td>
<td>Median **</td>
<td>87</td>
<td>91</td>
</tr>
<tr>
<td>ED - NF90 (5bar)</td>
<td>Maximum **</td>
<td>97</td>
<td>99</td>
</tr>
</tbody>
</table>

(*) Fen: fenobucarb; Iso: isoprothiolane; Pre: pretilachlor; Cond: Conductivity

(**) Maximum and median designate the synthetic solutions containing salts at the maximum value and the median value.

(‡) Energy consumption is calculated corresponding with experiment conditions at a fixed treatment time of 15 min (so the recovery was different for each one)
In general, the coupling processes involving NF270 consume less energy than those with NF90. The reason is that the pore size of NF270 is larger than that of NF90 resulting in a much higher permeability. Nevertheless, the retention efficiency is much better for processes involving NF90 membrane.

An advantage of NF-ED system is reducing the risk of fouling for the ED stage by the formation of precipitate at the ion exchange membrane surface when the concentration of divalent ions in water is too high. However, the real concentration of these ions in the surface water resources of the MD has no effect on the efficiency of ED, as was demonstrated in section 4.3.3.

As mentioned previously, the increase of the salt content in the input solution (feed) not only costs more energy, but also affects the efficiency of removing pesticides by NF stage. Therefore the application of ED as a pretreatment process for the NF to control the salt content in the water input is completely workable. The efficiency of removing pesticides is increased by the application of ED stage before NF stage. Moreover, this also reduces the energy consumption compared to NF-ED system in both cases of water inputs because the osmotic pressure of feed solution decreases when salt content decreases due to the ED stage (see Table 5-2).

It is important to consider that the efficiency of the appropriate hybrid system should respect the VN guideline requirement for drinking water. Even if the coupled processes involving NF270 membranes consume much less energy than those with NF90, the concentration of certain species in the product water is too high especially for the maximum salt concentration effluent.

Regarding to the efficiency of removing pesticides, the rejection of three pesticides (fenobucarb, isoprothiolane and pretilachlor) by ED-NF270 is 87, 91 and 99 %, respectively. Thus this system is capable of eliminating these pesticides in water at concentration up to 1µg/L for each type to be in compliance with the EC guideline value (0.1 µg/L). Basing on the results of Toan et al., the concentration of these three pesticides in surface water at An Long, which is the most pesticide polluted area, was at 1.43, 11.24 and 1.05 µg/L for the maximum values; at 0.11, 2.72 and 0.06 for the median values, respectively. Accordingly, this system cannot thoroughly treat isoprothiolane and fenobucarb at their maximum concentrations and isoprothiolane at its median concentration.

About desalination performance, this system cannot also remove Na\(^+\) and Cl\(^-\) to the satisfactory level, as described above. However, this can easily be overcome by increasing the operation time in ED stage to get 70% of salinity removal (instead of 50% in this experiments)
before connecting with NF. In contrast, the ED-NF90 system can almost completely eliminate the three kinds of pesticides even at maximum concentrations and desalination to a satisfactory standard. However, the energy consumption is five times higher than the ED-NF270 system.

In summary, the above studies suggest that the ED-NF90 system is best suited to treat surface water contaminated salinity and pesticides in the MD. However, it is necessary to optimize the treatment for reducing energy consumption. This will be further discussed in section 5.3.3.

5.3.3 Optimizing the NF process

Most of the experiments presented previously have been realized at a water recovery below 12%. As the energy consumption is expressed as the energy required producing one cubic meter of water (SEC), the water recovery rate has a deep impact on this parameter. In order to optimize the energy consumption in NF process, the water recovery should be increased. The energy consumption will decrease as the recovery increases (see equation (5-1)). The high energy consumption in previous studies (Table 5-2) is attributed to the low recovery factor reached after 15 min of operation (<3% and 10% for NF90 and NF270, respectively). However, the increase of recovery leads to the decrease of the rejection performance, due to increase of solute concentration in the feed. These two features must be evaluated to achieve an optimal recovery value. The objective of this part is to study the impact of water recovery on the energy consumption and NF efficiency.

5.3.3.1 Effect of recovery on permeate flux

The experimental and calculated permeate flux for the two feed solutions as a function of recovery is shown in Figure 5-5. From a general point of view, the permeate flux declines by increasing the recovery.
Moreover, it should be noted that the final flux in case of the Max50 is 42.1 (L/m$^2$.h), higher than the lowest value recommended similar to the specific value of the manufacture.

5.3.3.2 Effect of recovery on the NF efficiency and energy consumption

As mentioned previously, the water recovery of the NF process will change the feed solution concentration and thus will affect the NF efficiency and energy consumption. In order to monitor the evolution of the feed solution and process efficiency, many factors, such as conductivity, ion concentration of feed and permeate, rejection rate of ion and pesticide and water flux were evaluated. Firstly, the results of energy consumption and conductivity of the feed and permeate as a function of recovery are shown in Figure 5-6 for both Med50 and Max50 feed solution. It was observed that the energy consumption is going down rapidly during the first 20% of recovery. After this value, the energy consumption only reduces slowly with the increase of the recovery. This decrease is expected during the optimization of NF process. Nevertheless, to choose a good recovery, the product water quality must be considered.
Figure 5-6: The energy consumption and conductivity of the feed and permeate as a function of recovery for a) the Med50 and b) Max50

For the conductivity of the feed and permeate, both of them increase with the increase of the water recovery (Figure 5-6). Thus the rejection of the ions slightly decreases for both feed solutions treated, especially in Na\(^+\) and Cl\(^-\) rejection (Figure 5-7). On the other hand, the ion rejection of NF90 is very high (> 85%). It once again confirms that the NF is a crucial choice for treatment of synthetic river water.
Figure 5-7: The rejection of ions as a function of recovery for a) the Med50 and b) Max50

Figure 5-8 shows the evolution of the permeate quality, the energy consumption and the Cl\(^-\) and Na\(^+\) ion concentration of permeate as a function of the water recovery. The concentration of each ion present in permeate are shown in Table 5-3 and Table 5-4 for Med50 and Max50, respectively. In general, the ion concentration in the permeate increases with the water recovery increase which result in an increase of conductivity. For the divalent ions, since their rejection is very high while their feed concentration is low, their residues are always under VN guideline for both Med50 and Max50 solution, even at 80% of recovery.
Figure 5-8: The energy consumption and concentration of Cl$^-$ and Na$^+$ ion in the permeate as a function of recovery for a) the Med50 and b) Max50

For monovalent ions, it can be seen in Figure 5-8 that the concentration of Cl$^-$ in the permeate exceeds the VN guideline after 60% and 40% of recovery for the Med50 and Max50 solution, respectively. In case of Na$^+$, the recovery values in order to meet the VN guideline are higher than that of Cl$^-$, such as recovery as high as 80% and 50% may meet the requirements for the Med50 and Max50 solution, respectively. According to the VN guideline, the optimal value selected for water recovery will depend on chloride concentration in the permeate, which is the least retained species by NF90.

The optimal value of recovery for the NF90 process can be chosen at 50% for the Med50 solution and 30% for the Max50 solution. The energy consumption is respectively 0.8 and 1.7 (kWh/m$^3$)
at applied pressure of 12 and 15 bar, respectively. However, this consumption can be reduced when a lower pressure is applied to obtain 50 or 30% of recovery, because the applied pressure in experiments was set in order to reach 80% of that. Depending on the feed composition at the given recoveries (Table 5-3 and Table 5-4), the calculation by Nanoflux® software gives that the applied pressure should be 9 and 10 bar for the case of the Med50 and Max50, respectively. Thus, the energy consumption to obtain 50 or 30% of recovery for these solutions is 0.6 and 1.2 (kWh/m³), respectively (Calculated by equation (5-1)).

Furthermore, a more precise optimization could be realized in order to determine the condition for both ED and NF. In this case, ED was fixed at 50% of TDS removal. Higher TDS removal in ED can allow reaching higher water recovery for NF.

Table 5-3: The ion concentration in the permeate of the Med50 filtration experiment

<table>
<thead>
<tr>
<th>Y (%)</th>
<th>Cond. (mS/cm)</th>
<th>Na⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.42</td>
<td>58.7</td>
<td>5.4</td>
<td>1.1</td>
<td>103</td>
<td>9.3</td>
</tr>
<tr>
<td>10</td>
<td>0.39</td>
<td>55.6</td>
<td>4.6</td>
<td>1.1</td>
<td>97</td>
<td>7.2</td>
</tr>
<tr>
<td>20</td>
<td>0.36</td>
<td>53.6</td>
<td>3.6</td>
<td>1.0</td>
<td>93</td>
<td>4.4</td>
</tr>
<tr>
<td>31</td>
<td>-</td>
<td>79.2</td>
<td>6.2</td>
<td>1.6</td>
<td>136</td>
<td>22.6</td>
</tr>
<tr>
<td>41</td>
<td>0.70</td>
<td>102</td>
<td>8.4</td>
<td>2.0</td>
<td>174</td>
<td>17.2</td>
</tr>
<tr>
<td>51</td>
<td>0.90</td>
<td>132</td>
<td>11.5</td>
<td>2.5</td>
<td>227</td>
<td>25.3</td>
</tr>
<tr>
<td>60</td>
<td>1.07</td>
<td>158</td>
<td>13.4</td>
<td>3.2</td>
<td>269</td>
<td>29.9</td>
</tr>
<tr>
<td>70</td>
<td>0.92</td>
<td>-</td>
<td>8.3</td>
<td>1.9</td>
<td>-</td>
<td>15.2</td>
</tr>
<tr>
<td>82</td>
<td>1.24</td>
<td>203</td>
<td>10.0</td>
<td>2.3</td>
<td>339</td>
<td>16.3</td>
</tr>
</tbody>
</table>
Chapter 5 || Nanofiltration and electrodialysis coupling

Table 5-4: The ion concentration in the permeate of the Max50 filtration experiment

<table>
<thead>
<tr>
<th>Y (%)</th>
<th>Cond. (mS/cm)</th>
<th>Na⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.78</td>
<td>114</td>
<td>10.5</td>
<td>1.2</td>
<td>200</td>
<td>13.8</td>
</tr>
<tr>
<td>10</td>
<td>0.78</td>
<td>115</td>
<td>10.3</td>
<td>1.2</td>
<td>202</td>
<td>12.9</td>
</tr>
<tr>
<td>20</td>
<td>0.88</td>
<td>130</td>
<td>11.1</td>
<td>1.2</td>
<td>227</td>
<td>13.6</td>
</tr>
<tr>
<td>30</td>
<td>1.01</td>
<td>152</td>
<td>12.2</td>
<td>1.2</td>
<td>264</td>
<td>14.7</td>
</tr>
<tr>
<td>41</td>
<td>1.22</td>
<td>179</td>
<td>14.8</td>
<td>2.6</td>
<td>310</td>
<td>14.6</td>
</tr>
<tr>
<td>51</td>
<td>1.56</td>
<td>232</td>
<td>18.8</td>
<td>3.4</td>
<td>406</td>
<td>19.0</td>
</tr>
<tr>
<td>60</td>
<td>2.06</td>
<td>315</td>
<td>23.9</td>
<td>3.6</td>
<td>540</td>
<td>26.7</td>
</tr>
<tr>
<td>70</td>
<td>3.00</td>
<td>476</td>
<td>34.5</td>
<td>4.4</td>
<td>814</td>
<td>44.5</td>
</tr>
<tr>
<td>78</td>
<td>5.30</td>
<td>833</td>
<td>68.9</td>
<td>8.6</td>
<td>1433</td>
<td>98.7</td>
</tr>
</tbody>
</table>

These choices can be confirmed by the pesticide removal efficiency plotted in Figure 5-9. In case of the Max50 feed solution (Figure 5-9 (b)), the rejection of fenobucarb, isoprothiolane and pretilachlor at 30% of recovery was 96, 99.7, 96.8 %, respectively. It shows that these pesticides at the maximum concentration (as mentioned in section 5.3.2) can be efficiently removed in order to respect the EC guideline.

In the case of the Med50 solution, the rejection of these pesticides at 50% of recovery was somewhat lower than the values of the Max50 at 30% of recovery, but in the range of determination errors (about ± 3%). However, it is enough to treat them at maximum concentration to meet the EC guideline.
Figure 5-9: The rejection of pesticides as a function of recovery for a) the Med50 and b) Max50

Another point to be noted is the relationship between the solution conductivity and the ion concentration in the permeate solution. As shown in the experimental data in Table 5-3 and Table 5-4, when the concentration of Na\(^+\) or Cl\(^-\) ion exceeds the VN guideline, the conductivity of solution also exceeds 1.0 mS/cm. Thus, the conductivity can be a semi-quantitative parameter to control the efficiency of the water treatment process. The advantage of this parameter is that conductivity can be measured easily and continuously. It is useful to give a quick assessment for the process performance. After that the concentration of each ion may be determined to confirm this assessment.
5.4 Conclusion

The goal of this chapter is to study and propose solutions for the treatment of the complex surface water from the MD containing both high salinity and pesticides. In order to face this challenge, a hybrid process coupling NF and ED was proposed. ED was selected specifically for treating salinity whereas NF has for objective the removal of both pesticides and salinity. Four different treatment options have been studied such as NF270 – ED, NF90 – ED, ED – NF270 and ED – NF90. Energy consumption and process efficiency were considered for each treatment option. The purpose of this part is to determine the best combination with the best operating conditions in order to obtain an energy-efficient process able to produce good water quality (regarding the Vietnamese regulation). Depending on the obtained results, we can conclude as follows.

The integration of NF before ED is attributed to be inefficient for pesticide removal, due to the effect of salts on the pesticide rejection, although salt removal can be easily controlled by the second stage using ED. The energy demand for such combination is higher than processes integrating ED before NF, especially in the case of NF90 – ED.

The integration of ED before NF as a pretreatment process gives the best results for both pesticide and salt removal. In comparison between the ED – NF90 and ED – NF270 processes, the process of ED – NF270 consumes less energy but the efficiency is not enough to respect the VN guideline. It cannot remove pesticides (at maximum of concentration) and salts at a satisfactory level. It was thus suggest that ED – NF90 process is the best option to treat surface water of the MD contaminated by both high salinity and pesticides. In this point of view, a more complete study was realized in order to determine the best operating conditions for pesticide and salt removal, minimizing energy consumption.

It was pointed out that the water recovery (Y) has a huge impact on both pollutant retention and energy consumption with an opposite effect. 50% and 30% of water recovery was found to be the optimal ratio for Med50 and Max50 solution, respectively. The energy consumption calculated is respectively 0.6 and 1.2 kWh/m$^3$ at pressure of 9 and 10 bar applied. The pesticide and salt removal efficiency at these recoveries was indicated that meet the VN guideline of salt and EC guideline for pesticide.

The best option proposed for treating this challenging water is ED – NF90 where ED will remove 50% of salinity before applying NF at a recovery rate ranging from 30 to 50%
(depending on the river quality). The ED stage will work at a constant applied voltage of 15 V and the diluate and concentrate flow rate of 0.5 mL/min.
Chapter 6

Conclusion
6 Conclusion

Access to clean water of people in the rural area of the MD is very difficult, although there is abundant surface water source. This source is facing up to many environmental problems, especially, salinity intrusion and pesticide pollution. Direct water consumption after a simple household treatment is not safe, while the piped-water is impossible to access or possible to access with a high water production cost. Moreover, the present technology applied in the water supply stations has been also indicated to be inefficient for the treatment of these kinds of pollutants. Thus, the main issue required to be addressed is an effective treatment process with a low water production cost.

The objective of this thesis was to investigate the coupling of NF and ED processes to treat some simulated river water samples to respect the drinking water guidelines. The composition of the model waters was designed for containing salts at the maximum and median concentration value of them in the MD surface water during the dry season and the three most frequently detected pesticides (fenobucarb, isoprothiolane and pretilachlor). The NF and ED were firstly studied separately in order to have a full understanding of the transport through membranes as well as the effect of main parameters on their performance. After that the coupled processes were evaluated to determine the best operating conditions for pesticide and salt removal, as well as minimizing energy consumption.

In the first part, the performance behavior of the NF270 membrane for eliminating four representative single salt solutions was evaluated by a series of membrane filtration experiments on a laboratory-scale pilot in various feed concentration and operating conditions. At the beginning, the NF270 membrane was chosen because of its high flux at low operating pressures, which satisfies the surface water treatment with low energy. These experiments have brought a deeper understanding of the influence of operating conditions on the membrane performance. For instance, the flux performance of NF270 depends on trans-membrane pressure, osmotic pressure as well as electro-viscosity effect. When the applied pressure increases, the flux will increase. On the other hand, an increase of the salt feed concentration provokes a shift of the minimum pressure enabling permeation and a decrease of the flux variation vs. applied pressure due to increase of electro-viscosity. In addition, the effect of pH on the flux is mainly relative to the change of effective membrane charge density. It means that the higher pH leads to a reduction in the permeate flux.
The rejection performance of NF270 depends on a complex combination of many factors, such as diffusive flow, convective flow, electric migration flow, as well as ion size (sieving exclusion) and electrostatic interactions between the membrane and ions (Donnan exclusion). The rejection increased with the increase of applied pressure and leveled off to the maximum value at high applied pressure. The effect of pH on the rejection can be explained by the Donnan exclusion, due to the membrane zeta potential change. However, the Donnan effect becomes less important for the ions which have large size and low diffusivity (for example \( \text{SO}_4^{2-} \) compared to \( \text{Cl}^- \) ion). The different rejection between \( \text{Mg}^{2+} \) (in \( \text{MgSO}_4 \)) and \( \text{Na}^+ \) (in \( \text{Na}_2\text{SO}_4 \)) ion could be explained by the high normalized membrane charge density for \( \text{MgSO}_4 \) in comparison with that for \( \text{Na}_2\text{SO}_4 \). The effect of feed concentration on rejection performance can be illustrated and explained by the GCE approximation. A decrease of the normalized membrane charge density, with increasing feed concentration causes a reduction of salt rejection.

In the second part, the efficiency of two NF membranes, NF90 and NF270, to remove the three chosen pesticides representative of the pollution in the surface water of the MD was investigated. The adsorption of pesticides used on the membranes was studied systematically to understand its effect on rejection. The NF90 membrane showed as a crucial choice for removing pesticide when its performance was better than that of NF270. In the single solution, the rejection of pesticides increased in a corresponding way with the molecular weight of pesticides. In the mixtures, fenobucarb rejection obtained was considerably higher than that of the single solution in case of NF270 while those of isoprothiolane and pretilachlor were similar within experimental errors in the two kinds of experiments. While the competitive absorption (static experiment) of pesticides on a membrane surface can be considered to be negligible, the difference on the fenobucarb rejection is caused by a hindrance effect by others. In the presence of salts, the rejection tended to reduce for all pesticides and membranes used, while the rejection of salts seemed to be independent of the presence of pesticides. Especially, there was an increase of pure water flux after each experiment with the presence of salts in both cases of the two membranes.

Modeling the pesticide rejection by using the Nanoflux® software shows that some supplementary solute-membrane and solute-solute interactions which can be reflected by the change of the effective pore size impact the pesticide rejection of NF membrane.

In the third part, the performance of ED process for removal of NaCl was evaluated by a series of experiments under various feed composition and operating conditions. Besides, in order to investigate the feasibility of coupling with NF of ED, the desalination experiments were
carried out with permeate solutions of NF processes, and also with the simulated river water samples representative of surface water found in the MD directly. The optimal conditions and the performance of ED process were evaluated depending on the operation time, the kinetic rate constant and the energy consumption.

The increase of applied cell voltage, an important operating parameter leads to a quicker salt removal process. However, the best voltage obtained was 15V (for the given stack configuration) because the limiting current is exceeded and the transport of ions does not increase at higher voltage. Reversely, the energy consumption as the applicer voltage increased. This increase was faster for NaCl solution of 0.25 mol/L in comparison with that of 0.05 and 0.1 mol/L. This means that the current efficiency for the more concentrated solution is lower than that of the diluate ones. The presence of divalent cations caused an increase of the time operation, due to their lower mobility. However, there was no precipitate or fouling observed at their concentration up to 0.05 mol/L.

The flow rate increase may cause a reduction of boundary layer thickness and the concentration polarization as well as a decrease of ion residence time at the membrane, hence it impact to operation time reversely. Depending on the flow rate and concentration of ions, one of these two effects becomes dominant. Besides, it was demonstrated that the ion exchange capacity limit of the membranes is not reached at the highest concentration of NaCl studied (0.25 mol/L), NF permeate 1 as well as at the maximum concentration simulated river water. Thus ED process can be applied for these kinds of solutions directly without fouling observed.

In the last part, the integration of NF and ED was studied for the treatment of the complex surface water from the MD containing both high salinity and pesticides. The membrane process efficiency was evaluated by monitoring both treatment efficiency and energy consumption. Four different treatment options have been studied including NF270 – ED, NF90 – ED, ED – NF270 and ED – NF90 the combination giving the best performance in terms of pollutant removal and energy consumption.

The integrations of NF before ED are not recommended in this study due to their less efficiency for pesticide removal and higher energy consumption. When ED was used as a pretreatment process before NF, the process performance is better for both pesticide and salt removal. In that, the ED – NF90 process appears to be the best option to treat surface water contaminated by both high salinity and pesticides in the MD because the ED – NF270 process cannot remove pesticides (maximum of concentration) and salts at a satisfactory level. However,
its energy consumption needs to be minimized by increasing the water recovery. The water recovery of 50% and 30% was found to be the optimal ratio for Med50 and Max50 solution. This value of recovery cannot be increased more due to the reduction of pollutant retention. Actually beyond these recovery values, the passage of $\text{Na}^+$ and $\text{Cl}^-$ becomes too high to fulfill the VN guideline.

In summary, the best option proposed for treating this challenging water is ED – NF90 where ED will remove 50% of salinity before applying NF at a recovery rate ranging from 30 to 50% (depending on the river quality). The ED stage will work at a constant applied voltage of 15 V and the diluate and concentrate flow rate of 0.5 mL/min (for the setup configuration was used in chapter 4).

**Future work**

These conclusions of the thesis are a prerequisite for the development of a corresponding technology to apply for surface water treatment in the MD. However, to apply this technology in practice, some following study should be carried out:

- Using Nanoflux® software to simulate and understand more on the rejection of pesticides by the NF membrane.
- Optimizing the desalination process by electrodialysis
- Validating the coupling process to treat the real surface water in the Mekong Delta in consideration of the membrane fouling by the natural organic matter (NOM)
- Design a demonstrator pilot to apply in a rural area for family-sized plant
Reference


Reference


[105] M. a Rodrigo, N. Oturan, and M. a Oturan, “Electrochemically assisted remediation of


Appendix

The result of the pesticide rejection modeling by the Nanoflux® software

**Single Pesticide**

- **NF270**
- **NF90**

No adjust

- \( r_p \) adjust

- \( r_p + L_{eff} \) adjust
Appendix

Mix pesticide – without salt

NF270

No adjust

$ r_p $ adjust

$ r_p + L_{eff} $ adjust

NF90

$ r_p $ adjust

$ r_p + L_{cf} $ adjust
Appendix

Mix pesticide + Salt Cmed

NF270

No adjust

NF90

$p_r$ adjust

$p_r + L_{eff}$ adjust
Mix pesticide + salt Cmax

NF270

No adjust

$J \nu$ (l/h m$^2$)

$\nu_{\text{opt}}$

$r_p$ adjust

$r_p - L_{\text{eff}}$ adjust

NF90

No adjust

$J \nu$ (l/h m$^2$)

$\nu_{\text{opt}}$

$r_p$ adjust

$r_p - L_{\text{eff}}$ adjust
Appendix

The thesis summary in French
L’accès à l’eau potable est un des plus importants problèmes que l’on rencontre partout dans le monde même dans les pays riches en eau. Par exemple, les provinces côtières du Delta du Mékong (DM) subissent des périodes alternées d’inondations et de sécheresse. De plus, le changement climatique à l’origine d’une diminution de la pluviométrie et d’intrusion d’eau salée affecte gravement la qualité des eaux de la région. Les principales sources de pollution proviennent des déchets humains et des rejets des élevages de poissons, bétail et volaille. La pollution aux pesticides peut s’avérer un problème sérieux dans certaines zones. La détérioration de la qualité des eaux dans le DM et l’absence d’accès à l’eau potable dans les communes rurales entraîne une augmentation des maladies d’origine hydrique liées à la salinité, la présence de microorganismes et de polluants organiques. L’objectif de ce travail a consisté à examiner dans quelle mesure la technologie membranaire peut permettre de produire de l’eau potable de qualité. L’étude a porté sur les eaux saumâtres contenant des pesticides. Deux solutions modèles synthétiques ont été choisies pour représenter les eaux de surface du DM. Le dessalement et l’élimination des pesticides ont été réalisés en utilisant la nanofiltration (NF) couplée à l’électrodialyse. Le logiciel Nanoflux® a été utilisé pour interpréter les performances de deux membranes de NF (NF90 et NF270). Par ailleurs, la consommation d’énergie des deux procédés couplés a été estimée en fonction de la qualité de l’eau d’alimentation. Toutes ces données seront utilisées pour concevoir un démonstrateur pour la production familiale d’eau potable.

Mots clés : Technologie membranaire, traitement des eaux, dessalement, pesticide, électrodialyse, nanofiltration.
1 Introduction

1.1 Les objectifs de cette étude sont les suivants.

1. Etudier les technologies membranaires de nanofiltration (NF) et d’électrodialyse (ED) pour traiter des eaux saumâtres contenant des pesticides.

2. Quantifier les performances du couplage de la NF et de l’ED pour traiter solutions modèles d’eaux représentatives des eaux de surface trouvées dans le Delta du Mékong (DM).

3. Concevoir un démonstrateur pilote pour la purification d’eaux pour une utilisation familiale dans les zones rurales avec une estimation de la consommation d’énergie et du coût de la production d’eau.

1.2 Plan de l’étude

Les différents points abordés pour atteindre les objectifs énoncés ci-dessus sont les suivants:

- Revue de l’état actuel des connaissances relatif à la pollution des eaux de surface et l’utilisation des ressources en eaux dans le DM. A partir de ces données, détermination de la composition modèle d’échantillons d’eaux à traiter au laboratoire et la description des technologies membranaires sélectionnées (Chapitre 1)

- Etude de l’élimination des sels par NF en utilisant la membrane NF270 (Chapitre 2)

- Etude de l’élimination des pesticides utilisés dans le DM par NF en utilisant les membranes NF270 et NF 90 (Chapitre 3)

- Dessalement par ED d’eaux saumâtres représentatives des eaux de surface trouvées dans le DM (Chapitre 4)

- Couplage de la NF et de l’ED pour traiter des échantillons d’eaux synthétiques modèles représentatives des eaux de surface trouvées dans le DM dans le but de concevoir un démonstrateur pilote (Chapitre 5).

1.3 Le Delta du Mekong

La ressource en eaux de surface joue un rôle important dans le développement socio-économique de la région. Il est non seulement le facteur primordial de la production agricole mais aussi la motivation du développement industriel. Dans le même temps, les eaux de surface sont la principale source d’eau des activités domestiques incluant l’eau de boisson.

Bien que les eaux de surface soient une ressource en eau facilement accessible et bon marché, sa qualité est confrontée à de nombreux problèmes environnementaux, tels que les périodes alternées d’inondation et de sécheresse, le changement climatique conduisant à des diminutions de chutes d’eau et des intrusions salines plus importantes pendant les saisons sèches. Par ailleurs, la pollution provenant des activités humaines (déchets domestiques, des élevages de poissons et de volailles ou encore de l’usage inconsideré de pesticides) constitue également une menace pour son utilisation domestique.

1.4 Objectif du traitement

Cette étude s’intéresse à la salinité et aux pesticides contenus dans les eaux de surface avec pour objectif de les traiter par des procédés membranaires pour respecter les directives de l’eau de boisson. Les autres paramètres tels que la matière solide en suspension et la contamination microbienne peuvent être enlevés de l’eau par les traitements habituellement pratiqués par les gens comme les opérations de filtration et d’ébullition, ou encore avec par le procédé de traitement membranaire.

Du fait de la difficulté en termes d’éloignement géographique, nos études s’arrêteront à l’échelle laboratoire avec le traitement d’échantillons modèles d’eau représentatifs des eaux de surface trouvés dans le DM. La composition des solutions modèles utilisées et le rapport des cations sont résumés dans le tableau 1-1.

En ce qui concerne la composition en pesticides, nous les avons choisis en se basant sur les résultats de recherche de Toan et al. [2] et Chau et al. [3]. Ces auteurs ont montré que trois sortes de pesticides (insecticide, fongicide and herbicide) spécifiques sont le plus fréquemment détectés dans les eaux de surface du DM : le Fenobucarb, l’Isoprothiolane et le Pretilachlor. De plus, ils possèdent des propriétés physiques similaires à celles d’autres pesticides comme par exemple leurs masses molaires variant du plus léger le Fenobucarb (207.3 g mol$^{-1}$) au plus lourd le Pretilachlor (311.8 g mol$^{-1}$).
Tableau 1-1: Composition des eaux synthétiques modèles utilisées dans nos expériences.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Rapport en masse des cations (%)</th>
<th>Concentration massique maximum* (mg/L)</th>
<th>Concentration massique médiane* (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>13887</td>
<td>3184</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1763</td>
<td>449</td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>83.4</td>
<td>7316</td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3.38</td>
<td>297</td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>13.2</td>
<td>1160</td>
<td></td>
</tr>
</tbody>
</table>

(*) Maximum and médiane désigne les solutions synthétiques contenant les sels à leur valeur maximum et médiane.

2 Performance de la membrane NF270 pour la rétention des sels

Dans ce chapitre, les performances de la membrane NF 270 pour l’élimination des sels sont évaluées par une série d’expériences de séparation en utilisant des compositions variées de solutions d’alimentation et sous des conditions opératoires variées. Les paramètres incluant le pH, la concentration en sels de l’alimentation et la pression trans-membranaire, ont été étudiés par leur influence sur le flux de perméat et l’efficacité de la rétention des sels. Les résultats obtenus serviront à établir une base de données dans le logiciel Nanoflux® pour prédire la rétention des sels par la membrane NF270.

2.1 Matériels and méthodes

2.1.1 Dispositifs expérimentaux

Les expériences de filtration ont été réalisées avec un pilote de filtration présenté en Figure 2-1. La membrane était placée à l’intérieur de la cellule Osmonics Sepa CF II Sterlitech Corp., Kent, WA). Des coupons de 155 cm² (19 cm x 14 cm) avec une surface utile de 140 cm², ont été découpés dans une feuille de membrane plane.
2.1.2 Membrane NF270

La membrane NF270 de la Société Dow Filmtec a été choisie pour réaliser cette étude. En effet, cette membrane a été conçue pour le traitement des eaux de surface et de forage avec des débits de perméat élevés à des pressions de travail relativement basses. La membrane NF270 a été caractérisée par son angle de contact à l’eau, son potentiel zêta et sa perméabilité à l’eau pure. Ces déterminations ont été réalisées sur de coupons de membranes après la procédure de conditionnement.

2.2 Résultats

2.2.1 Caractérisation de la membrane

La valeur moyenne de l’angle de contact à l’eau obtenue est de 53±3°. Cette valeur montre que la membrane NF270 possède une surface plutôt hydrophile qui permet une utilisation aisée pour le traitement de solutions aqueuses. Le point isoélectriques de la membrane NF270 a été trouvé égal à pH 3.1 dans les conditions opératoires utilisées (KCl 10⁻³ M). La perméabilité à l’eau pure moyenne est de 15.8 ± 1.0 L/m².h.bar dans nos conditions de filtration.

2.2.2 Effet de la pression appliquée sur les rejets de sels et les débits de perméat.

Le rejet de solutions de sels simples à une concentration de 10⁻² mol/L par la membrane NF270 en fonction de la pression appliquée entre 3 et 15 bar à pH 6 augmente lorsque la pression appliquée augmente pour se stabiliser à une valeur de rétention qui dépend du sel considéré. Le rejet atteint une valeur quasi stationnaire pour des pressions supérieures à 5 bar. Pour des raisons
économiques, le procédé pourrait donc être réalisé à des pressions de 5 à 7 bars pour cette concentration en sels.

Le rejet expérimental des 4 sels étudiés (NaCl, Na$_2$SO$_4$, CaCl$_2$ and MgSO$_4$) en fonction du débit de perméat est bien modélisé par le logiciel Nanoflux$^\circledR$ dans les conditions opératoires (Figure 2-2) considérées ci-dessus avec des déviations standard entre les valeurs expérimentales et calculées de 0.00403, 0.00299, 0.00576 and 0.00447, respectivement.

Figure 2-2: Le rejet expérimental des 4 sels étudiés (NaCl, Na$_2$SO$_4$, CaCl$_2$ and MgSO$_4$) en fonction du débit de perméat à une concentration de 10$^{-2}$ mol/L par la membrane NF270 à pH 6

Les débits de perméat pour les mêmes expériences montrent une variation linéaire avec la pression appliquée dans tous les cas.

2.2.3 Effet du pH sur le rejet en sel et les débits de perméat

Il a été trouvé la séquence suivante pour la rétention des sels simples par ordre décroissant $R_{Mg^{2+}(MgSO_4)} \approx R_{Na^+(Na_2SO_4)} > R_{Na^+(NaCl)} > R_{Ca^{2+}(CaCl_2)}$ à pH 6 et pH 10 alors qu’à pH 3 la séquence devient $R_{Mg^{2+}(MgSO_4)} > R_{Na^+(Na_2SO_4)} > R_{Ca^{2+}(CaCl_2)} > R_{Na^+(NaCl)}$. Cet effet peut être expliqué par la théorie du mécanisme d’exclusion de Donnan. En effet, à pH 3 la charge de la membrane est devenue positive ce qui entraîne un rejet plus important des cations divalents.

Le débit de perméat décroit quand le pH devient plus alcalin pour tous les sels étudiés. Cet effet est attribué à une augmentation de la valeur absolue de la densité de charge effective de la membrane à des valeurs de pH élevées.
2.2.4 Effet de la concentration en sels de l’alimentation sur les débits de perméat et les rejets de sels

Le débit de perméat diminue lorsque la concentration de la solution d’alimentation augmente 10^{-3} mol/L à 10^{-1} mol/L à pH 6 sur la même gamme de pression appliquée que précédemment. Cet effet a été attribué à une augmentation de la pression osmotique $P$ quand la concentration en sels de l’alimentation augmente.

Le rejet tend à décroître avec l’augmentation de la concentration (Figure 2-3). Cette tendance peut clairement être mise en évidence dans le cas du rejet de NaCl qui atteint 85, 78 et 53 % à 15 bar pour des concentrations de 10^{-3} mol/L, 10^{-2} mol/L et 10^{-1} mol/L, respectivement.

Figure 2-3: Effet de la concentration en sels de l’alimentation sur les rejets de sels: (a) NaCl, (b) Na\n\_2SO\_4, (c) CaCl\_2 and (d) MgSO\_4 (à pH 6)
3 Elimination des pesticides utilisés dans le Delta du Mékong par NF

Le besoin d’études systématiques sur l’effet de l’adsorption, la présence d’ions inorganiques et d’autres paramètres sur le rejet des pesticides par les membranes de NF est évident au vu des résultats contradictoires trouvés dans la littérature. Le but de ce chapitre est d’étudier les performances de deux membranes de NF (NF90 et NF270) pour l’élimination de quelques pesticides le plus fréquemment détectés dans les eaux de surface du DM. Le Fenobucarb (Fen), l’Isoprothiolane (Iso), et le Pretilachlor (Pre) ont été choisis comme les molécules les plus représentatives des pesticides se trouvant dans cette région. L’adsorption de ces pesticides sur la surface membranaire a été systématiquement étudiée pour comprendre son effet sur le rejet. Des solutions synthétiques contenant des concentrations en sel similaires à celles rencontrées dans eaux réelles de la rivière ont été utilisées pour étudier l’influence des sels sur le rejet des pesticides.

3.1 Matériels

Membrane sélectionnée

Deux types de membranes planes de NF ont été utilisés dans cette étude : la NF270 et la NF90.

Propriétés des pesticides ciblés

Le Fenobucarb, l’Isoprothiolane, et le Pretilachlor sont représentatifs de trois des principales familles de pesticides utilisées dans le DM: insecticide, fongicide and herbicide. La structure moléculaire et les propriétés physicochimiques des pesticides choisis sont présentés dans le Tableau 3-1.

Tableau 3-1: La structure moléculaire et les propriétés physicochimiques des pesticides ciblés.
3.2 Résultats

3.2.1 Rejet dans le cas de solutions simples de pesticide

Le rejet des pesticides par la membrane NF90 est généralement plus élevé que celui obtenu avec la membrane NF270. Des retentions similaires et plus grandes que 95 % sont observées dans le cas de NF90 pour tous les pesticides. Ces valeurs expérimentales peuvent être expliquées en première approximation par le seuil de coupure (MWCO) de la membrane. Il est plus petit dans le cas de la membrane NF90 (200 Da) que le $M_w$ de tous les pesticides (Tableau 3-2), alors que la membrane NF270 possède une taille de pores plus large avec un MWCO de 300 Da de la même taille que le pesticide le plus grand.

3.2.2 Effet de la coexistence de plusieurs pesticides dans la solution d'alimentation

Dans le cas de la membrane NF270 (Figure 3-1 (a)), l’influence de la coexistence de plusieurs pesticides dans la solution d’alimentation sur le rejet s’est avérée différente selon la taille des solutés. La rétention du Fenobucarb obtenue dans les expériences avec un mélange de pesticides est beaucoup plus importante que celle obtenue dans le cas des experiences de solutions simples, alors que celles de l’Isoprothiolane et du Pretilachlor sont tout à fait similaires (à l’intérieur du domaine d’erreur expérimental). Il a été montré que l’adsorption compétitive sur la surface membranaire peut être considérée comme négligeable au moins dans les expériences statiques. Puisque le Pretilachlor et l’Isoprothiolane dans une moindre mesure sont fortement retenus, ils peuvent former une couche dynamique à la surface de la membrane entrainant une gêne stérique pour le passage du Fenobucarb au travers de la membrane.

Dans le cas de la NF90 membrane (Figure 3-1 (b)), La rétention n’apparaît influence par la présence des autres pesticides. Cette observation peut s’expliquer par le fait que l’efficacité de l’élimination des trois pesticides est similaire.
3.2.3 Rejet des pesticides à partir des eaux synthétiques représentatives de l’eau de rivière

Si on compare les différentes matrices, il peut être observé que les rétentions des pesticides dans l’eau pure sont généralement plus élevées que celles obtenues dans les eaux synthétiques dans tous les cas de figure (pesticides ou les membranes utilisées) (Figure 3-2). Ce résultat peut être attribué à une dilatation apparente des pores en présence de concentration élevée de sels. Les résultats de la modélisation de la rétention des pesticides par le logiciel Nanoflux® confirment l’hypothèse d’élargissement des pores.

Figure 3-2: Le rejet des pesticides par la membrane (a) NF270 et (b) NF90 dans les différentes matrices (no salt: l’eau pure; Med et Max: des eaux synthétiques représentatives de l’eau de rivière à les concentrations de la salinité médiane et maximale)
La présence de pesticides n’a pas d’impact significatif sur la rétention des ions même si des différences ont été trouvées dans le cas de la membrane NF270 pour les concentrations élevées en sels. Par ailleurs, la rétention des ions monovalents tend à décroître quand leur concentration dans la solution d’alimentation augmente pour les deux membranes étudiées.

4 Dessalement par ED

Dans ce chapitre, la performance de l’étape d’ED pour l’élimination du NaCl a été évaluée par une série d’expériences réalisées dans différentes conditions opératoires. De plus, afin d’évaluer la faisabilité du couplage de la NF et de l’ED, des expériences de dessalement ont été effectuées en utilisant les perméats des solutions de NF obtenues dans le chapitre précédent ainsi que des solutions synthétiques modèles représentatives des eaux de surface trouvées dans le MD.

4.1 Equipement et membranes

Le montage d’ED consiste en un générateur de courant continu, un réservoir pour le concentrat et un pour le diluat, un réservoir de rinçage des électrodes d’un volume de 2L, 3 pompes à entrainement magnétique (Siebec M7, Angleterre) chacune équipée d’un débit mètre et de vannes pour contrôler le débit des solutions dans les compartiments des cellules d’ED.

Les expériences d’ED ont été réalisées avec une cellule PCell ED 64-004 (PCA GmbH, Heusweiler, Allemagne). La cellule est équipée de 7 membranes échangeuses d’anions et de 8 membranes échangeuses de cations, et d’une paire d’électrodes (anode et cathode). La surface active des membranes était de 64 cm². Des espaceurs en plastique sont placés entre les membranes pour former des trajets de flux d’une largeur de 0.5 mm. Les deux électrodes sont en titane recouvert de Pt/Ir. Les membranes échangeuses de cations et d’anions utilisées dans l’empilement sont des membranes standard PC-SK et PC-SA (PCA GmbH, Heusweiler, Allemagne).

4.2 Résultats

4.2.1 Effet de la concentration

Dans cette partie, les expériences d’ED ont été réalisées avec des solutions de NaCl à des concentrations de 0,05, 0,1 et 0,25 mol/L avec un différence de potentiel de 5V et un débit de 0,5
L/min. Le temps nécessaire pour extraire 90 % du sel augmente en même temps que la concentration de la solution d’alimentation avec des valeurs de 66, 74 et 99 min, respectivement.

La consommation électrique montre la même tendance du fait d’un temps opératoire plus long (de 1,1 à 4,5 kWh/m$^3$) alors que la constante de vitesse cinétique est inversement proportionnelle en diminuant de 0,035 à 0,022 1/min. Dans le cas de la solution à 0,1 mol/L en NaCl, ce qui est similaire à la conductivité de l’eau saumâtre à traiter, la consommation énergétique est de 2,5 kWh/m$^3$ pour atteindre les contraintes réglementaires de l’eau de boisson.

4.2.2 Influence de la différence de potentiel

L’augmentation de la différence de potentiel conduit à un abaissement du temps nécessaire pour atteindre une baisse de 90 % du taux de sel dans le cas d’une concentration initiale de 0,05 mol/L en NaCl dans la solution d’alimentation (66, 33, 28 et 25 min pour 5, 10, 15, and 20 V, respectivement). Les mêmes tendances sont observées pour des concentrations initiales de 0,1 et 0,25 mol/L. Ce phénomène peut simplement s’expliquer par le fait que le flux d’ions au travers de la membrane échangeuse d’ions suit la loi de Nernst – Planck. Cependant, le temps de l’opération ne change pas significativement pour des voltages supérieurs à 15 V.

On peut noter que le temps est à peu près identique pour les trois solutions dans le cas d’un voltage supérieur à 10V. Cette observation indique que la capacité limite d’échange des membranes n’est pas atteinte à la concentration de 0,25 mol/L. Par conséquent, on peut conclure que l’ED peut être appliquée dans cette gamme de concentrations.

4.2.3 Influence du débit

En règle générale, la durée de l’ED peut être abaissée par une augmentation du débit dans la cellule. Cette hypothèse a été vérifiée dans le cas des 3 perméats de NF en augmentant le débit de 0,25 à 1,5 L/min. Par exemple, le temps nécessaire pour éliminer 90 % de la salinité du perméat de NF 1 (la conductivité est 24 mS/cm) prend 36, 24, 21 et 20 min pour des débits, respectivement, de 0,25, 0,5, 1,0 et 1,5 L/min. Le dessalement par ED des perméats de NF 2 et 3 (la conductivité est 12 et 5 mS/cm) suit la même tendance avec, respectivement, un abaissement de 36 à 14 min et de 33 à 13 min.

4.2.4 Dessalement des perméats de NF par ED

Le dessalement des perméats de NF a été réalisé en appliquant différents voltages pour évaluer l’application de ce procédé à ces eaux. Comme précédemment, l’augmentation de la
Différence de potentiel conduit à une diminution du temps de dessalement. A partir de 15 V, la durée de l’opération plafonne à des valeurs de 24, 21 et 20 min pour, respectivement, les perméats 1, 2 et 3. Cela signifie que dans tous les cas, on peut éliminer 90 % de la salinité des perméats de NF pour une durée d’ED de 25 min maximum.

4.2.5 Dessalement des eaux de rivière modèles par ED

Les expériences de dessalement ont été réalisées avec les deux solutions modèles choisies représentatives des eaux du MD en utilisant une différence de potentiel de 15 V et un débit de 0,5 L/min. Les résultats obtenus montrent que l’ED marche bien avec la solution de concentration médiane (TDS = 5,6 g/L). Dans ce cas la réduction de salinité atteint 90 % après 30 min avec une énergie consommée de 5,3 kWh/m$^3$. La constante cinétique est de 0,083 min$^{-1}$, ce qui est plus faible que dans le cas des solutions de NaCl 0,1 mol/L qui a une conductivité similaire. Ce phénomène a été attribué à la présence de cations divalent.

Dans le cas de la solution à la concentration maximum (TDS = 24,4 g/L), cela prend 43 min pour éliminer 90% de la salinité avec une énergie consommée de 24,7 kWh/m$^3$. La durée de l’opération est seulement 1,5 fois celle de la concentration médiane alors que la concentration en sels est 4 fois supérieure. Cependant, l’énergie consommée est 5 fois celle de la concentration médiane.

Par ailleurs, il faut mentionner qu’aucun précipité ni colmatage des membranes n’a été observé quel que soit le cas étudié. Ainsi, ces résultats démontrent que l’ED peut être appliquée même sur les eaux de rivière directement.

5 Le couplage NF - ED

5.1 Intégration des procédés NF–ED

Puisque les performances de rejet des pesticides par le procédé de NF sont affectées par la présence de sels, particulièrement dans le cas des fortes concentrations, un procédé hybride intégrant la NF suivie par une étape d’ED ne sera pas suffisamment performant pour atteindre la norme imposée pour l’eau potable.

La possibilité d’appliquer directement l’ED aux solutions synthétiques représentatives des eaux réelles a été démontrée en section 4.2.5. C’est pourquoi, un procédé intégré couplant l’ED suivie de la NF a été examiné dans les deux de figure des eaux considérées. La solution de
concentration médiane a été d’abord dessalée dans l’étage d’ED puis envoyée sur l’étage de NF équipé de la membrane NF270, alors que la solution de concentration maximum a été nanofiltrée sur la membrane NF 90 après l’étage d’ED. Dans chaque cas, les expériences ont été réalisées en mode « batch ».

De manière à réduire la consommation énergétique de l’étage d’ED, la réduction de la concentration en sel a été fixée à 50% (mesurée par conductivité) au lieu de 90 % comme effectuée précédemment.

5.1.1 Résultats

5.1.1.1 Performance de l’ED

Il a été observé que la concentration des ions dans le diluat diminuait avec le temps de dessalement de façon similaire dans les deux cas indiquant que tous les ions sont transportés à travers les membranes échangeuses d’ions par l’action du champ électrique même si leur cinétique d’extraction peut être différente.

5.1.1.2 Performance de la NF

La rétention des pesticides durant l’étage de NF dans le procédé intégré ED-NF a été évalué par comparaison avec la rétention du procédé de NF seule (NF directe) en utilisant la même membrane mais des pressions appliquées différentes. La performance de la NF pour éliminer les pesticides est bien meilleure pour les deux solutions modèles utilisées lorsque l’ED est utilisée comme prétraitement. Ce résultat était attendu puisque la rétention des pesticides est meilleure à faible salinité.

5.1.1.3 Qualité de l’eau produite

Dans cette partie, la qualité de l’eau produite a été évaluée sur la base de la concentration en ions par rapport à la directive vietnamienne pour l’eau portable publiée par le Ministère de la Santé (MOH), QCVN 01:2008/BYT.

La qualité de l’eau produite dans le cas du couplage ED-NF (NF90) est conforme avec la directive vietnamienne pour tous les paramètres. Par contre, les concentrations du Na⁺ et du Cl⁻ dans l’eau produite lors du couplage ED-NF (NF270) excédaient celles de la directive d’un facteur 1,7 et 2,2 respectivement pour la concentration médiane et la concentration maximum bien que le taux de solides dissous (TDS) restait légèrement en dessous de la norme.
5.2 Comparaison entre les procédés

De manière à choisir le traitement approprié en utilisant le couplage ED et NF, quatre combinaisons ont été considérées à savoir NF270 - ED, NF90 - ED, ED - NF270 et ED - NF90. Pour chaque combinaison, l’efficacité du procédé et la consommation énergétique ont été évaluées pour les deux types d’eaux modèles étudiés (concentration médiane et maximum).

L’application de l’ED comme procédé de prétraitement de manière à contrôler le taux de sels dans la solution d’entrée de l’étage de NF est tout à fait réaliste. L’efficacité pour l’extraction des pesticides est augmentée par la diminution de la concentration des sels liée à l’étage d’ED. De plus, la consommation énergétique de la NF est abaissée comparé à l’intégration inverse de la NF avant l’ED du fait que la pression osmotique de l’alimentation décroît grâce à l’élimination des sels par l’étage d’ED.

Pour ce qui est de de la performance, le couplage ED-NF (NF90) permet d’éliminer pratiquement complètement les trois sortes de pesticides et d’abaisser les sels à un taux satisfaisant même pour la solution à la concentration maximum. Cependant, la consommation énergétique est environ 5 fois supérieure à celle du système ED-NF (NF270). Il s’avère donc nécessaire d’optimiser le traitement de manière à réduire cette consommation. Ce point est discuté dans la section suivante.

5.3 Optimisation de l’étape de NF (NF90)

La plupart des expériences présentées jusqu’ici ont été réalisées avec un taux de récupération d’eau au maximum de 12 %. Comme la consommation d’énergie est exprimée par m$^3$ d’eau produite (SEC), le taux de récupération a un impact important sur ce paramètre. Par ailleurs, l’augmentation du taux de récupération entraîne une diminution des performances de rétention des sels par la membrane due à l’augmentation de leur concentration dans l’alimentation. L’influence du taux de récupération a, par conséquent, été étudiée afin d’optimiser l’étape de la NF en termes de consommation d’énergie et d’efficacité de dessalement.

5.3.1 Résultats

Il a été observé que la consommation énergétique par m$^3$ d’eau produite du procédé de NF pour les deux solutions d’alimentation Med50 et Max50, diminue rapidement pendant les premiers 20 % du taux de récupération. Au-delà de cette valeur, elle ne diminue que lentement.
Cette diminution est attendue durant le procédé d’optimisation de l’étape de NF. Néanmoins, pour choisir le bon taux de récupération, un autre point important est la qualité de l’eau produite.

La teneur résiduelle des ions divalents se situe toujours (aussi bien pour Med50 et Max50) en dessous des valeurs recommandées par la norme vietnamienne même à des taux de récupération de 80%. Ceci s’explique par leur rétention élevée et leur concentration faible dans la solution d’alimentation.

Par contre, dans le cas des ions monovalents, la situation est différente. La concentration des ions Cl$^-$$^-$ excède la limite de la directive vietnamienne pour des valeurs de taux de récupération de l’ordre de 60 et 40% respectivement pour Med50 et Max50 alors que cette situation se rencontre dans le cas des ions Na$^+$ pour des valeurs respectivement de 80 et 50%. On peut donc en conclure que la valeur maximale du taux de récupération est fixée par la concentration des ions Cl$^-$$^-$ dans le perméat qui est l’espèce la moins retenue par la membrane NF90.

La valeur optimale du taux de récupération dans le cas de l’étape de NF (en utilisant la membrane NF90) doit être choisie à environ 50% pour Med50 et 30% pour Max50. Les consommations énergétiques sont respectivement de 0,8 et 1,7 kWh/m$^3$ à des pressions appliquées de 12 et 15 bar, respectivement. Ces choix ont été confirmés par les performances d’élimination des pesticides dans les mêmes conditions. Dans le cas de Max50, l’élimination de Fenobucarb, Isoprothiolane et Pretilachlor à 30% de taux de récupération est respectivement de 96, 99,7 et 96,8%. Ces valeurs montrent que les pesticides à la concentration maximum (voir section 5.2) peuvent être éliminés efficacement pour respecter les normes européennes.

6 Conclusion

L’accès à une eau propre pour les populations vivant dans les zones rurales du DM est très difficile en dépit de l’abondance de l’eau de surface. Cette ressource doit faire face à de nombreux problèmes environnementaux, spécialement les intrusions salines et la pollution par les pesticides. Un usage direct après un traitement sommaire n’est pas sûr, alors que la distribution publique d’eau est soit non disponible soit possible mais à un coût de production trop élevé. Par ailleurs, la technologie actuellement employée dans les stations d’approvisionnement d’eau est inefficace pour le traitement de dessalement et d’élimination des pesticides. Ainsi, la principale
question qui doit être résolue est d’obtenir un traitement efficace avec un coût de production raisonnable pour les populations locales.

L’objectif de cette thèse est d’étudier le couplage des technologies NF et ED pour traiter des échantillons simulant l’eau du Mékong de manière à obtenir une eau respectant la directive vietnamienne sur l’eau potable. La composition des eaux modèles a été conçue pour contenir les sels aux concentrations maximale et médiane rencontrées dans les eaux de surface du DM durant la saison sèche ainsi que les 3 pesticides les plus fréquemment détectés (Fenobucarb, Isoprothiolane et Pretilachlor). La NF et l’ED ont été dans un premier temps étudiés séparément pour bien comprendre le transport aux travers des membranes et les effets des principaux paramètres du procédé sur leur performance. Puis le couplage des procédés a été évalué pour déterminer les meilleurs conditions opératoires pour l’élimination des sels et des pesticides et, d’autre part, pour une consommation énergétique minimale.

Dans la première partie, les performances de la membrane NF270 ont été évaluées dans une série d’expériences à l’échelle laboratoire pour éliminer quatre solutions de sels représentatifs (NaCl, CaCl$_2$, Na$_2$SO$_4$, MgSO$_4$) à des concentrations d’alimentation et dans des conditions de filtration variables. La membrane NF270 avait été choisie pour les flux élevés obtenus à faibles pression de filtration, ce qui est en fait le bon choix pour un traitement d’eau de surface à faible énergie. Ces expériences ont apporté une connaissance approfondie des conditions opératoires sur les performances membranaires de NF. Par exemple, le flux de perméat dépend de la pression transmembranaire, de la pression osmotique mais aussi des effets liés à l’électro-viscosité. Quand la pression appliquée augmente, le flux augmente. D’un autre côté, une augmentation de la concentration de sels dans l’alimentation provoque un décalage de la pression minimum permettant un début de perméation et une diminution de la pente flux en fonction de la pression reliée à l’augmentation de l’électro-viscosité. De plus, l’effet du pH sur le flux est principalement fonction de la densité de charge effective de la membrane. Cela signifie que les pH élevés conduisent à une réduction des flux de perméat.

La rétention par la NF270 dépend d’une combinaison complexe de nombreux facteurs, tels que les flux diffusif et convectif, le flux de migration électrique mais aussi la taille des ions (exclusion stérique) et les interactions électrostatiques entre la membrane et les ions (exclusion de Donnan). La rétention augmente avec l’augmentation de la pression appliquée jusqu’à atteindre un plateau à pression appliquée élevée. L’effet du pH sur la rétention peut s’expliquer par le
changement des charges de surface de la membrane mise en évidence par la variation du potentiel zêta. Cependant, l’effet Donnan devient moins important pour les ions de grande taille et de faible diffusivité (par exemple \( \text{SO}_4^{2-} \) comparé à \( \text{Cl}^- \)). La différence de rétention entre les ions \( \text{Mg}^{2+} \) (\( \text{MgSO}_4 \)) et \( \text{Na}^+ \) (\( \text{Na}_2\text{SO}_4 \)) pourrait s’expliquer par une densité de charges normalisée plus élevée pour \( \text{MgSO}_4 \) que pour \( \text{Na}_2\text{SO}_4 \). L’effet de la concentration de l’alimentation peut être expliqué par l’approximation « Good Co-ion Exclusion ». La réduction de la rétention des sels est alors due à une diminution de densité de charge normalisée de la membrane.

Dans une seconde partie, les performances de l’élimination des pesticides choisis par les membranes NF90 et NF270 ont été étudiées. L’adsorption de ces pesticides sur les membranes a été systématiquement examinée pour voir son effet sur la rétention. La membrane NF90 s’avère un le meilleur candidat pour l’élimination des pesticides car ses performances sont meilleures que celles de la membrane NF270. Dans les solutions simples, la rétention augmente dans le même sens que les masses molaires des pesticides. En mélange, l’élimination du Fenobucarb est considérablement plus élevée que dans le cas des solutions simples dans le cas de NF270 alors que celles de l’Isoprothiolane et du Pretilachlor restent similaires dans la marge des erreurs expérimentales. Puisque l’adsorption compétitive sur la surface de la membrane s’est avérée négligeable, la différence observée pour la rétention du Fenobucarb a été interprétée par un effet stérique induit par la rétention des autres pesticides. En présence de sels, la rétention tend à diminuer pour les pesticides étudiés et membranes utilisées. La rétention des sels, par contre, semble indépendante de la présence des pesticides. La modélisation de la rétention des pesticides avec le logiciel Nanoflux® montre que des interactions supplémentaires soluté-membrane et soluté-soluté qui se traduisent par un changement apparent de la taille de pore, pourraient être impliquées dans le mécanisme de transport de ces composés.

Dans une troisième partie, la performance du procédé d’ED pour l’élimination du \( \text{NaCl} \) a été évaluée par une série d’expériences dans des différentes conditions de composition de l’alimentation et de paramètres opératoires. Pour examiner la faisabilité du couplage avec la NF, des expériences de dessalement par ED ont été réalisées avec des perméats de NF mais aussi avec des eaux modèles représentatives des eaux de surface trouvées dans le DM. Les conditions optimales et les performances de l’ED ont été caractérisées en termes de temps opératoire, de constante cinétique et de consommation énergétique.
L’augmentation du voltage appliqué dans la cellule conduit à l’élimination plus rapide du sel. Cependant, le meilleur voltage obtenu a été de 15 V (pour une configuration donnée d’empilement de membranes) du fait que la capacité limite d’échange est atteinte impliquant que le transport d’ions n’augmente plus au-delà de cette valeur. Inversement, la consommation énergétique augmente avec le voltage appliqué. Cette augmentation est d’autant plus grande que la concentration en sel est élevée. Cela signifie que le courant efficace est plus bas pour les solutions les plus concentrées. La présence des ions divalents entraine une augmentation du temps de l’opération dû à leur plus faible mobilité. Cependant, il doit être noté qu’aucune précipitation ou colmatage n’ont été observé pour des concentrations allant jusqu’à 0.05 mol/L.

Une plus grande vitesse de circulation des solutions peut entraîner une réduction de l’épaisseur de la couche limite et de la concentration de polarisation aussi bien qu’une diminution du temps de résidence des ions près de la membrane d’où un impact sur le temps de l’opération. Dépendant du flux de circulation et de la concentration des ions, un de ces deux effets devient dominant. Il a ainsi été démontré que la capacité limite d’échange n’est pas atteinte à la concentration la plus élevée de NaCl étudiée (0.25 mol/L) aussi bien que pour les perméats de NF obtenus à partir de la solution modèle à la concentration la plus haute. Ainsi, le procédé d’ED peut être appliqué directement dans le cas de ces solutions sans l’observation de colmatage.

Dans la dernière partie, l’intégration de la NF et de l’ED a été étudiée pour le traitement de solutions complexes contenant à la fois une forte salinité et des pesticides. Le couplage a été évalué à la fois par son efficacité du traitement et sa consommation énergétique. Quatre différentes options ont été envisagées NF270 – ED, NF90 – ED, ED – NF270 et ED – NF90. L’intégration de la NF avant l’ED n’est pas recommandée du fait de sa moindre efficacité pour l’élimination des pesticides et sa consommation énergétique plus élevée. Quand l’ED a été utilisé comme prétraitement avant la NF, la performance du procédé est meilleure à la fois pour l’élimination des pesticides et des sels. Le couplage ED – NF270 ne permet pas d’éliminer les pesticides (à la concentration maximum) et les sels à un niveau satisfaisant. Par contre, le procédé combinant l’ED et NF90 apparaît comme la meilleure option pour traiter les eaux de surface contaminées à la fois par une haute salinité et les pesticides. Cependant, sa consommation énergétique doit être minimisée en augmentant le taux de récupération d’eau. Des taux de récupération de 50 et 30 % ont été trouvés comme le rapport optimal pour les solutions Med50 et Max50. Cette valeur n’a pas pu être augmentée plus du fait de l’augmentation de la concentration.
des ions dans le rétentat qui diminue l’efficacité de l’élimination de la pollution. En fait, au-delà de ces valeurs de récupération, le passage des ions Na\(^+\) et Cl\(^-\) devient trop haut pour satisfaire à la réglementation vietnamienne sur l’eau potable.

En résumé, la meilleure option proposée pour ces eaux très difícile à traiter est le couplage ED – NF90 dans lequel l’ED (15 V et vitesse de circulation de 0.5 mL/min) élimine 50% de la salinité avant l’utilisation de la NF avec un taux de récupération de 30 à 50% (dépendant de la qualité de l’eau à traiter).