Removal of Chemicals of Emerging Concern and Mass Transfer Modeling in a Nanofiltration Membrane Process

Carlyn Higgins
University of Central Florida

Part of the Environmental Engineering Commons

Find similar works at: https://stars.library.ucf.edu/etd2020
University of Central Florida Libraries http://library.ucf.edu

This Doctoral Dissertation (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations, 2020- by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

STARS Citation
REMOVAL OF CHEMICALS OF EMERGING CONCERN AND MASS TRANSFER MODELING IN A NANOFILTRATION MEMBRANE PROCESS

by

CARLYN J. HIGGINS
B.S. Env.E. University of Central Florida, 2016
M.S. Env.E. University of Central Florida, 2017

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Civil, Environmental, and Construction Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Summer Term
2020

Major Professor: Steven J. Duranceau
©2020 Carlyn J. Higgins
ABSTRACT

An investigation of 1,4-dioxane and enantiomeric ibuprofen mass transfer in a nanofiltration (NF) membrane process has been completed. Pilot-scale experiments using a 267 gallon per minute (gpm) split-feed, center-port NF process treating pH 6.5 groundwater revealed a consistent 12 percent removal of 1,4-dioxane despite the variable feed concentration (180 nanograms per liter (ng/L) to 38,400 ng/L) when the water flux and temperature were held constant. Bench-scale, flat-sheet NF membrane experiments treating pH 4.0 synthetic water displayed a 34.5 to 49.5 percent removal of racemic ibuprofen. Removal values were dependent on feedwater concentration (1 to 1,500 microgram per liter (µg/L)), pH, pressure, and water matrix. Although 1,4-dioxane was not found to exhibit adsorptive tendencies, as much as 25 percent of racemic ibuprofen adsorbed onto the metal surfaces of the testing equipment. Mass balances determined that ibuprofen’s S-enantiomer was primarily responsible for the adsorption. Density functional theory (DFT) computations exposed a 6.4 cubic angstrom (Å³) smaller molecular volume and 1.10 x 10⁻²⁹ coulomb-meters (Debye) longer dipole moment of S-ibuprofen than R-ibuprofen, which could explain the S-enantiomers stronger affinity to stainless-steel equipment components. The rejection of S-ibuprofen was consistently greater than R-ibuprofen, postulated by the dissimilar polarity of the two molecules outlined by DFT calculations. Feedwater ibuprofen concentration, pH, and operating pressure affected ibuprofen adsorption onto the equipment and membrane components. Contact angle measurements revealed a direct relationship between membrane hydrophobicity and adsorbed ibuprofen concentration. Langmuir and Freundlich isotherms accurately modeled S-ibuprofen adsorption. Therefore, at least 24 hours of equilibration is required prior to conducting hydrophobic solute membrane rejection studies. Additionally, application of the Homogeneous
Solution Diffusion Model (HSDM) was found to provide accurate predictions of 1,4-dioxane and R-ibuprofen permeate content based on statistical analysis; however, the model was less predictive for the S-enantiomer due to adsorptive tendencies of the molecule.
To my family and friends, whose unwavering love and encouragement has driven me to accomplish more than I’ve ever thought possible.
ACKNOWLEDGMENTS

The research conducted in the following document could not have been accomplished without the support of many individuals. I would like to specially thank my committee chair Dr. Steven J. Duranceau, who not only provided the opportunity for this work, but offered considerable time, expertise, and sagacity throughout this endeavor. I would also like to thank my other committee members, Dr. Anwar Sadmani, Dr. Woo Hyoung Lee, and Dr. Melanie Beazley for their time, erudition, and helpful recommendations in review of this research. I would like to thank Melissa Saint James for her management and supervision in the laboratory. I would also like to thank other UCF personnel, including Pete Alferis, Tedra Johnson, Lorna Rodriguez, and Erin Ward for their support. Thanks are given to UCF Water Quality Engineering Research Team alumni, including Samantha Black, Angela Rodriguez, David Yonge, and Paul Biscardi for their guidance and tutelage of sampling and laboratory procedures.

Thanks is sincerely owed to the UCF Water Quality Engineering Research Team, including Daniel Whalen, Jessica Cormier, Courtney Powell, Tulsi Shukla, Paula Campesino, Zach Protas, Devon Higgins, Frances Martinez-Marrero, Nino Stea, and Eric Barnes for their direct assistance in this work. Thanks is also offered to Kunal Olimattel for his help with the bench-scale, flat-sheet experimental setup, and Josh Lee for his help with the HPLC. and I would like to specially to thank Tulsi Shukla for her encouragement and empowerment through this endeavor. Special thanks are also owed to Daniel Whalen for his never-ending support, wisdom, practical suggestions, and entertaining memes about graduate school. I could not have completed this degree without my “PhD pal” by my side for the journey.
This work would not have been made possible without support provided by the Town of Jupiter Utilities (17403 Central Boulevard, Jupiter FL 33458, USA). Thanks are given to the Town of Jupiter personnel, including David Brown, Amanda Barnes, Rebecca Wilder, Paul Jurczak, Tony Fogel, Sara Ouly, and Gary Schultze. The assistance of the Town’s operations staff is also appreciated. Thanks is given to Tommy Carr and Eugene Aman from Pace Analytical (8021-6 Philips Hwy Jacksonville, FL 32256, USA). Support provided by Sterlitech, Inc (22027 70th Ave S, Kent, WA 98032, USA), especially Kensen Hirohata is greatly valued. Thanks is also given to Laura Gallindo and Steven Coker from Dupont Water Solutions (7600 Metro Blvd, Edina, MN 55439, USA) for providing FilmTec NF270 flat-sheet membrane coupons.

Finally, I would like to thank my family and friends. Mom and Dad (Karen and John), thank you for your profound belief in my abilities and financial assistance throughout my educational journey. Grandma (Francine), thank you for your inspiring wisdom about graduate school and your career. Devon, thank you for your support as well keeping the Higgins name in the UCF Water Quality Engineering Research group. Dylan, thank you for your patience, comfort, and encouragement. Amy and Maddie, thank you for your friendship, knowledge, and serenity. Your uplifting support, encouragement, and love has helped in more ways than I can count.
TABLE OF CONTENTS

LIST OF FIGURES ...................................................................................................................... xii

LIST OF TABLES ...................................................................................................................... xvii

LIST OF EQUATIONS ................................................................................................................ xx

LIST OF ACRONYMS AND OTHER ABBREVIATIONS ........................................................... xxiii

CHAPTER 1. INTRODUCTION ..................................................................................................... 1

Objectives ................................................................................................................................... 2

Previous Publications ................................................................................................................ 4

CHAPTER 2. LITERATURE REVIEW .......................................................................................... 5

Membrane Technologies for Potable Treatment ...................................................................... 5

Overview of Nanofiltration Membrane Process ..................................................................... 5

Overview of Chemicals of Emerging Concern ....................................................................... 10

Chemical of Emerging Concern Removal by Nanofiltration ................................................. 12

Selected Solutes in Research ................................................................................................. 18

Ibuprofen ............................................................................................................................... 18

1,4-Dioxane ........................................................................................................................... 21

Mass Transfer Modeling ........................................................................................................ 23

CHAPTER 3. MATERIALS AND METHODS ............................................................................ 29
CHAPTER 4. RESULTS AND DISCUSSION

Bench-Scale Ibuprofen Enantiomer Removal Experiments

Adsorption of Ibuprofen onto Flat-Sheet Equipment

Adsorption of Enantiomeric Ibuprofen onto Flat-Sheet Equipment and Membrane in Operation

Determination of Membrane Operational Characteristics
Adsorption of Enantiomeric Ibuprofen onto Flat-Sheet Equipment and Membrane in Operation ............................................................................................................................... 61
Adsorption Isotherm Models ............................................................................................................. 72
Rejection of Enantiomeric Ibuprofen in a Bench-Scale, Flat-Sheet NF Process .................. 85
Pilot-Scale 1,4-Dioxane Removal Experiments ................................................................................. 108
Surficial Groundwater Water Quality ............................................................................................. 109
Determination of Solute Mass Transfer Coefficient .......................................................................... 110
Determination of Experimental Variables ........................................................................................ 111
1,4-Dioxane Rejection Prediction ..................................................................................................... 112
1,4-Dioxane Permeate Concentration Prediction ............................................................................. 113

CHAPTER 5. SUMMARY AND CONCLUSIONS .................................................................. 118

Summary ........................................................................................................................................... 118
Conclusions ...................................................................................................................................... 120

CHAPTER 6. RECOMMENDATIONS ..................................................................................... 125

APPENDIX A. DESALINATION AND WATER TREATMENT COPYRIGHT PERMISSION LETTER ........................................................................................................ 128

APPENDIX B. EXAMPLE CALCULATIONS ........................................................................... 130

APPENDIX C. HSDM AND HSDM-FT MODEL DERIVATION ........................................... 143

APPENDIX D. MASS BALANCE CALCULATIONS ..................................................................... 149

x
APPENDIX E. QUALITY CONTROL .............................................................................................. 156
  Accuracy Charts ......................................................................................................................... 157
  Precision Charts .......................................................................................................................... 158
APPENDIX F. ADSORPTION ISOTHERM MODELS ........................................................................ 161
APPENDIX G. REGRESSION MODEL DERIVATION USING MICROSOFT EXCEL ........ 168
REFERENCES .................................................................................................................................. 172
LIST OF FIGURES

Figure 2-1: Membrane process schematic mass balance ................................................................. 7
Figure 2-2: CEC rejection variables from NF processes ................................................................. 15
Figure 2-3: Ibuprofen enantiomers ............................................................................................... 19
Figure 2-4: Ibuprofen speciation based on log K_a value (4.4) ....................................................... 20
Figure 3-1: A photograph of the bench-scale, flat-sheet unit ....................................................... 30
Figure 3-2: Flat-sheet bench-scale unit schematic (recycle mode)............................................... 31
Figure 3-3: Flat-sheet bench-scale unit schematic (permeate collection mode) ......................... 32
Figure 3-4: Experimental variables studied for ibuprofen removal via NF process ..................... 34
Figure 3-5: Experimental variables studied for ibuprofen mass balance with flat-sheet equipment ....................................................................................................................................................... 34
Figure 3-6: A photograph of SPE in process (left) and Organomation N-EVAP® nitrogen gas evaporator (right) ................................................................................................................................................................................................................................................................. 37
Figure 3-7: A photograph of the Perkin Elmer HPLC .................................................................. 38
Figure 3-8: HPLC ibuprofen enantiomer chromatogram .............................................................. 38
Figure 3-9: A photograph of the ramé-hart goniometer ................................................................ 39
Figure 3-10: Standard curves of R- (left) and S- ibuprofen (right) ............................................... 40
Figure 3-11: Schematic of Town’s split-feed, center-port NF process ........................................... 42
Figure 3-12: A photograph of the NF pilot unit ............................................................................ 43
Figure 3-13: A photograph of the full-scale NF trains (left) and pilot-scale NF unit (right) (Photo by Duranceau, 2015) ................................................................................................................................................................................................................................................................................. 43
Figure 3-14: Diffusion-based modeling procedure ....................................................................... 46
Figure 4-1: Adsorbed R- and S- ibuprofen onto flat-sheet equipment (pH 4, temperature 20±1°C) ................................................................. 53

Figure 4-2: Relationship between R- and S- ibuprofen adsorption onto metal flat-sheet equipment ....................................................................................................................................................... 54

Figure 4-3: S-ibuprofen bound to COX-2 (Orlando et al., 2014) (left); S-ibuprofen bound to stainless-steel surface (right) ............................................................................................................... 55

Figure 4-4: Bond dipoles and dipole moment of R- (left) and S- (right) ibuprofen (Photo output by GAMESS software) ...................................................................................................................... 57

Figure 4-5: R- and S- ibuprofen adsorption onto flat-sheet equipment as a function of pH ........ 58

Figure 4-6: Membrane pure water flux as a function of applied pressure (psi) ......................... 60

Figure 4-7: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 membrane (left) and TS40 membrane (right) in operation (pH 4, water flux 25 gal/ft²d, temperature 20±1°C) .... 62

Figure 4-8: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 membrane at 50 and 150 psi feed pressure ........................................................................................................................................ 64

Figure 4-9: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 (pH 4, water flux 70 gal/ft²d, temperature 20±1°C) ...................................................................................................................... 66

Figure 4-10: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 (left) and TS40 (right) membrane as a function of pH ...................................................................................................................... 68

Figure 4-11: Contact angle of dried NF270 and TS40 membranes as a function of adsorbed ibuprofen concentration (pH 4, water flux 25 gal/ft²d, temperature 20±1°C) ............................................. 69

Figure 4-12: Contact angle of dried NF270 and TS40 membranes as a function of feed water pH (water flux 25 gal/ft²d, temperature 20±1°C) ...................................................................................................................... 70
Figure 4-13: Contact angle of dried NF270 membranes as a function of adsorbed ibuprofen concentration (pH 4, water flux 70 gal/ft²d, temperature 20±1°C) .............................................................. 71

Figure 4-14: Adsorption isotherm curves of ibuprofen-equipment relationship ................................................. 77

Figure 4-15: Adsorption isotherm curves of ibuprofen-equipment-membrane relationship, NF270 (left), TS40 (right) (pH 4, water flux 25 gal/ft²d, temperature 20±1°C) .................................................. 80

Figure 4-16: Adsorption isotherm curves of ibuprofen-equipment-NF270 membrane relationship (pH 4, water flux 70 gal/ft²d, temperature 20±1°C) .................................................................................. 83

Figure 4-17: Rejection of R- and S- ibuprofen at pH 4 (water flux 25 gal/ft²d, temperature 20±1°C). ....................................................................................................................................................... 86

Figure 4-18: Rejection of R- and S- ibuprofen from NF270 membrane at 25 gal/ft²d (left) and 70 gal/ft²d (right) (pH 4, temperature 20±1°C) ................................................................................................. 88

Figure 4-19: Rejection of R- and S- ibuprofen from TS40 membrane at 25 gal/ft²d (pH 4, temperature 20±1°C) ............................................................................................................................. 88

Figure 4-20: Rejection of R- and S- ibuprofen at 50 and 150 psi operating pressure (pH 4, temperature 20±1°C) ............................................................................................................................. 90

Figure 4-21: Rejection of R- and S- ibuprofen as a function of pH for NF270 membrane (left), TS40 membrane (right) (water flux 25 gal/ft²d, temperature 20 ± 1°C) ................................................. 93

Figure 4-22: Water quality comparison between NGW (Town of Jupiter, left) and SGW (right) 95

Figure 4-23: Rejection of R- and S- ibuprofen from NF270 (left) and TS40 (right) membranes treating control, NGW, and SGW matrices ........................................................................................................... 97

Figure 4-24: Predicted ibuprofen rejection using empirical model ................................................................. 101

Figure 4-25: Extent of ibuprofen overestimation from independent literature ............................................. 103
Figure 4-26: NF270 and TS40 membrane R- (left) and S- (right) ibuprofen solute flux as a function of change in concentration (pH 4, temperature 20 ± 1°C) .......................................................... 105

Figure 4-27: Actual vs. HSDM predicted R- and S- ibuprofen permeate concentration for NF270 (left) and TS40 (right) membranes ........................................................................................................ 106

Figure 4-28: 1,4-Dioxane solute flux as a function of change in concentration (pH 6.5, temperature 26°C; presented on log-log scale) ............................................................................................... 111

Figure 4-29: Average rejections for diffusion-based models .......................................................... 113

Figure 4-30: Actual vs. predicted 1,4-dioxane permeate concentration using HSDM and SH-HSDM (presented on log-log scale) ........................................................................................... 114

Figure 4-31: RPD range and RMSE for HSDM models ............................................................. 115

Figure E-1: R-ibuprofen spike control chart ............................................................................... 157

Figure E-2: S-ibuprofen spike control chart ............................................................................... 158

Figure E-3: R-ibuprofen duplicate RPD control chart ............................................................... 158

Figure E-4: S-ibuprofen duplicate RPD control chart ............................................................... 159

Figure E-5: R-ibuprofen duplicate I-stat control chart ............................................................... 159

Figure E-6: S-ibuprofen duplicate I-stat control chart ............................................................... 160

Figure F-1: Linearized Langmuir R- and S- ibuprofen isotherm plot of flat-sheet equipment . 162

Figure F-2: Linearized Freundlich R- and S- ibuprofen isotherm plot of flat-sheet equipment. 162

Figure F-3: Linearized Temkin R- and S- ibuprofen isotherm plot of flat-sheet equipment..... 163

Figure F-4: Linearized Langmuir R- and S- ibuprofen isotherm plot of NF270 membrane in operation ............................................................................................................................... 163
Figure F-5: Linearized Freundlich R- and S- ibuprofen isotherm plot of NF270 membrane in operation ................................................................. 164

Figure F-6: Linearized Temkin R- and S- ibuprofen isotherm plot of NF270 membrane in operation ..................................................................................................................................................... 164

Figure F-7: Linearized Langmuir R- and S- ibuprofen isotherm plot of TS40 membrane in operation ............................................................................................................................................... 165

Figure F-8: Linearized Freundlich R- and S- ibuprofen isotherm plot of TS40 membrane in operation ..................................................................................................................................................... 165

Figure F-9: Linearized Temkin R- and S- ibuprofen isotherm plot of TS40 membrane in operation ............................................................................................................................................... 166

Figure F-10: Linearized Langmuir R- and S- ibuprofen isotherm plot of NF270 membrane in high-pressure operation ............................................................................................................................................... 166

Figure F-11: Linearized Freundlich R- and S- ibuprofen isotherm plot of NF270 membrane in high-pressure operation ............................................................................................................................................... 167

Figure F-12: Linearized Temkin R- and S- ibuprofen isotherm plot of NF270 membrane in high-pressure operation ............................................................................................................................................... 167
LIST OF TABLES

Table 2-1: NF effectiveness in removing CECs ................................................................. 13
Table 2-2: Chemical properties of ibuprofen ................................................................. 20
Table 2-3: Chemical properties of 1,4-dioxane ............................................................. 22
Table 3-1: NF membrane properties ............................................................................. 31
Table 3-2: Experimental summary of ibuprofen rejection in bench-scale NF process ... 35
Table 3-3: Experimental summary of ibuprofen mass balance with flat-sheet equipment ... 36
Table 3-4: NF pilot unit operational parameters ........................................................... 44
Table 3-5: Experimental summary of 1,4-dioxane removal from pilot-scale NF process ... 45
Table 3-6: List of methods and equipment for water quality analysis ......................... 47
Table 4-1: DFT calculated energy and geometries of R- and S- ibuprofen ..................... 56
Table 4-2: NF membrane flat-sheet operational properties ............................................. 61
Table 4-3: Surface area calculations of flat-sheet equipment ......................................... 75
Table 4-4: Adsorption isotherm parameters of equipment-ibuprofen relationship ........ 77
Table 4-5: Error analysis for the adsorption equilibrium modeling of ibuprofen-equipment relationship ................................................................. 78
Table 4-6: Adsorption isotherm parameters of equipment-ibuprofen-membrane relationship at normal operating conditions (pH 4, water flux 25 gal/ft²d, temperature 20±1°C) ............... 79
Table 4-7: Error analysis for the adsorption equilibrium modeling of equipment-ibuprofen-NF270 membrane relationship ........................................................................................ 81
Table 4-8: Error analysis for the adsorption equilibrium modeling of equipment-ibuprofen-TS40 membrane relationship ................................................................................... 81
Table 4-9: Adsorption isotherm parameters of equipment-ibuprofen-membrane relationship at high-pressure operating conditions (pH 4, water flux 70 gal/ft²d, temperature 20±1°C) ............... 83
Table 4-10: Error analysis for the adsorption equilibrium modeling of ibuprofen onto flat-sheet equipment and NF270 membrane at high-pressure ................................................................. 84
Table 4-11: Hydrophobic CEC rejection at various pressures from independent literature ........ 92
Table 4-12: Rejection of water quality parameters from NF270 and TS40 flat-sheet membranes ....................................................................................................................................................... 96
Table 4-13: Contact angle and flat-sheet image of NF270 membrane treating control, NGW, and SGW matrices ........................................................................................................................................................... 99
Table 4-14: Ibuprofen rejection from independent literature .................................................. 102
Table 4-15: Membrane operational parameters for HSDM ....................................................... 105
Table 4-16: Statistical analysis of HSDM R- and S-ibuprofen permeate concentration .......... 108
Table 4-17: NF pilot feed and permeate water quality ............................................................... 110
Table 4-18: Operational variables from NF pilot for 1,4-dioxane rejection prediction .......... 112
Table 4-19: Statistical $t$-test data for 1,4-dioxane rejection prediction ..................................... 116
Table B-1: Example ERRSQ calculation .................................................................................... 139
Table B-2: Example RMSE calculation ...................................................................................... 141
Table B-3: Example $t$-value calculation .................................................................................. 142
Table D-1: NF270 R-ibuprofen 24 h concentrate mass balance RPD ........................................ 152
Table D-2: NF270 S-ibuprofen 24 h concentrate mass balance RPD ........................................ 153
Table D-3: TS40 R-ibuprofen 24 h concentrate mass balance RPD ........................................... 154
Table D-4: TS40 S-ibuprofen 24 h concentrate mass balance RPD ............................................... 154
LIST OF EQUATIONS

2-1 ................................................................................................................................................ 7
2-2 ................................................................................................................................................ 7
2-3 ................................................................................................................................................ 8
2-4 ................................................................................................................................................ 8
2-5 ................................................................................................................................................ 9
2-6 ................................................................................................................................................ 9
2-7 ................................................................................................................................................ 9
2-8 ............................................................................................................................................... 10
2-9 ............................................................................................................................................... 10
2-10 ............................................................................................................................................. 21
2-11 ............................................................................................................................................... 24
2-12 ............................................................................................................................................... 24
2-13 ............................................................................................................................................... 24
2-14 ............................................................................................................................................... 25
2-15 ............................................................................................................................................... 25
2-16 ............................................................................................................................................... 25
2-17 ............................................................................................................................................... 25
2-18 ............................................................................................................................................... 26
2-19 ............................................................................................................................................... 26
2-20 ............................................................................................................................................... 26
2-21 ............................................................................................................................................... 26

xx
C-3 ............................................................................................................................................... 145
C-4 ............................................................................................................................................... 145
C-5 ............................................................................................................................................... 147
C-6 ............................................................................................................................................... 147
C-7 ............................................................................................................................................... 148
D-1 ............................................................................................................................................... 150
D-2 ............................................................................................................................................... 150
### LIST OF ACRONYMS AND OTHER ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>effective area</td>
</tr>
<tr>
<td>b</td>
<td>Temkin isotherm equilibrium binding constant</td>
</tr>
<tr>
<td>CA</td>
<td>cellulose acetate</td>
</tr>
<tr>
<td>Ca, Ct</td>
<td>concentration of actual sample, theoretically calculated sample</td>
</tr>
<tr>
<td>CCL</td>
<td>Contaminant Candidate List</td>
</tr>
<tr>
<td>CEC</td>
<td>chemical of emerging concern</td>
</tr>
<tr>
<td>C_F, C_P, C_C, C_B</td>
<td>concentration in feed, permeate, concentrate, bulk stream</td>
</tr>
<tr>
<td>C_M</td>
<td>concentration at membrane surface</td>
</tr>
<tr>
<td>cm²</td>
<td>square centimeter</td>
</tr>
<tr>
<td>C_o, C_e</td>
<td>initial, equilibrium concentration</td>
</tr>
<tr>
<td>C_s, C_d</td>
<td>concentration of sample, duplicate</td>
</tr>
<tr>
<td>C_{s+sp}, C_{sp}</td>
<td>concentration of spiked sample, spike</td>
</tr>
<tr>
<td>Da</td>
<td>Dalton</td>
</tr>
<tr>
<td>D_h</td>
<td>hydraulic diameter</td>
</tr>
<tr>
<td>DI</td>
<td>deionized water</td>
</tr>
<tr>
<td>D_i</td>
<td>solute diffusivity</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
</tr>
<tr>
<td>EKA</td>
<td>electrokinetic analyzer</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>some of square errors</td>
</tr>
<tr>
<td>ft²</td>
<td>square feet</td>
</tr>
<tr>
<td>ft/d</td>
<td>feet per day</td>
</tr>
<tr>
<td>gal/d</td>
<td>gallons per day</td>
</tr>
<tr>
<td>gal/ft²d</td>
<td>gallons per square foot day</td>
</tr>
<tr>
<td>gal/h</td>
<td>gallons per hour</td>
</tr>
<tr>
<td>gal/m</td>
<td>gallons per minute</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
</tbody>
</table>
l/min  liter per minute
l/h    liter per hour
LWL    limit warning limit
m²     square meter
mg/L   milligram per liter
MF     microfiltration
MGD    million gallons per day
min    minute
m/s    meter per second
MWCO   molecular weight cut off
n⁻¹    Freundlich adsorption intensity constant
NGW    natural groundwater
NF     nanofiltration
ng/L   nanogram per liter
nm     nanometer
NOM    natural organic matter
NSAID  non-steroidal anti-inflammatory
NTP    net transmembrane pressure
PA     polyamide
PA-TFC polyamide thin-film composite
PD     pressure drop
Pr, Pr, Pc pressure of feed, permeate, concentration streams
psi    pounds per square inch
PZ     polypiperazine
QA/QC  quality assurance and quality control
Qf, Qp, Qc flow rate of feed, permeate, concentrate streams
qa     maximum solute adsorption capacity
qe     concentration of solute on surface
R      recovery
\( R^2 \)  
coefficient of determination

r  
rejection

\( R_e \)  
Reynolds number

\( R_L \)  
Langmuir separation factor

\( R_u \)  
universal gas constant

RMSE  
root mean square error

RO  
reverse osmosis

RPD  
relative percent difference

\( s_t \)  
standard deviation

\( S_c \)  
Schmidt number

SCADA  
supervisory control and data acquisition

SGW  
synthetic groundwater

\( S_h \)  
Sherwood number

SPE  
solid phase extraction

\( S_{\text{pre}}, S_{\text{post}} \)  
extracted sample with analyte, extracted blank followed by spike

\( S_{S/R} \)  
chiral selectivity

\( T_f, T_p, T_c \)  
temperature of feed, permeate, concentrate streams

Town  
Town of Jupiter Water Utilities

TDS  
total dissolved solids

UCF  
University of Central Florida

UCL  
upper control limit

UCMR  
Unregulated Contaminant Monitoring Rule

UF  
ultrafiltration

US  
United States

USEPA  
United States Environmental Protection Agency

UV\(_{254}\)  
ultraviolet absorption at 254 nanometers

UWL  
upper warning limit

V  
volume of aqueous solution

v  
velocity
VFD variable frequency drive
$V_i$ solute molar volume at normal boiling point
WTF water treatment facility
$x$ membrane channel width
$x_{ave}$ average
$y$ membrane channel height
$\Delta P$ transmembrane pressure differential
$\Delta \pi$ osmotic pressure differential
$\mu$ dynamic viscosity
$\mu g/cm^2$ microgram per square centimeter
$\mu g/L$ microgram per liter
$\mu m$ micrometer
$\mu S/cm$ microSiemans per centimeter
$\rho$ density
$\phi$ solvent association factor
$^\circ C$ degrees Celsius
CHAPTER 1. INTRODUCTION

A variety of organic and inorganic chemicals of emerging concern (CECs) originating from municipal, agricultural, and industrial wastewater sources are being found at increased frequency in drinking water supplies. These CECs include pharmaceuticals, antibiotics, steroids, hormones, flame retardants, perfluorinated compounds, personal care products, herbicides, and pesticides. While concentrations of emerging contaminants are extremely low, the effects on human and aquatic health due to persistent exposure are not well understood and therefore a source of concern. CECs have been detected at the nanogram per liter (ng/L) to milligram per liter (mg/L) in source water supplies. Contamination in water bodies has been linked to discharge of rudimentary wastewater treatment plants, poorly maintained sewers, septic tanks, landfills, or illegal disposal sites (Nghiem et al., 2005; Fawell & Ong, 2012). CECs have also been detected in potable water, indicating that conventional drinking water treatment may not provide the proper barriers from such chemicals (Glassmeyer et al., 2016; Furlong et al., 2017). As research regarding potential adverse effects of CECs progresses, regulatory action will likely follow suit. Therefore, there is an exigency to determine CEC removal capabilities of advanced drinking water treatment technologies.

Nanofiltration (NF) is a pressure driven membrane separation process that has shown promise in CEC rejection, while also utilizing less energy than its brethren technology reverse osmosis (RO), yielding an attractive option in water treatment applications (Choi et al., 2001; Duranceau & Taylor, 2011; Howe et al., 2012). As the molecular weight cut-off (MWCO) of a NF membrane is 200 Dalton (Da) or higher, it is postulated that significant rejection of CECs larger than that size
can be attained (Bellona et al. 2004; Wang et al., 2015). However, the MWCO does not account for solute charge, geometry, or other physiochemical properties. Research has suggested that NF CEC rejection can be variable and influenced not only by molecular weight, but also solute chemical properties, membrane properties, and operational properties (Comerton et al., 2008; Darvishmanesh et al., 2010). Therefore, the inherent complexity of CEC rejection by NF membranes should be elucidated.

Objectives

To scientifically contribute to the existing body of knowledge on membrane CEC removal capabilities, bench-scale and pilot-scale NF processes were utilized to determine rejection efficacy of enantiomeric ibuprofen and 1,4-dioxane. To obtain realistic rejection values akin to those experienced in application, natural water matrices were evaluated at the bench-scale and pilot-scale. The pilot-scale unit housed full-scale membranes dimensionally analogous to production scale operations. Specific objectives of this research included the investigation are focused on answering the following questions:

1. Do enantiomers exhibit similar or different rejection behavior?
2. How does feed water CEC concentration, operational pressure, feed water pH, or feed water matrix composition affect CEC rejection in a NF process?
3. Can existing diffusion-based models accurately predict NF CEC mass transfer?

The first question addresses a solute property (chirality) that has not been previously studied in evaluations of chemical behavior in a NF process. A chemical containing a carbon atom with four nonidentical substituents is considered chiral, and thus comprises two compounds that are non-
identical mirror images and hence non-superimposable, known as enantiomers. Although pairs of enantiomers contain identical chemical and physical properties, the geometric spatial arrangement differs. Enantiomers are known to demonstrate atypical behavior in medicinal applications. Therefore, it is hypothesized that enantiomers may exhibit deviant solute behavior in a NF process.

The second topic addresses the dependence of multiple variables on CEC rejection in a NF process. Although existing literature has suggested that feed water matrix properties can affect rejection, most studies have used synthetic water concoctions that are not truly representative of natural matrices. In addition, most studies typically conduct experiments with bench-scale equipment and appurtenances. It is recognized that operational pressure, feed water pH, and feed water matrix composition can impact the rejection of CECs in a NF process. Although bench-scale studies can provide some insight into mass transfer phenomenon, it is accepted that pilot-scale studies with natural water matrices will incur rejection values that align more closely with existing full-scale operation. To respond to the second interrogatory, a NF bench-scale process was utilized to ascertain the impacts of natural water on CEC rejection. In addition, an analogous pilot- and full-scale side-by-side process were operated and monitored while treating natural groundwater containing CECs of interest.

The third and final topic evaluates the ability of existing diffusion-based models to predict rejection of CECs in a NF process. Water purveyors can apply models to their respective membrane treatment systems to predict CEC rejection without conducting physical experiments using potentially hazardous chemicals. Model output along with other tools can ascertain the need for additional water treatment infrastructure in response to impending regulation.
Previous Publications

Part of Chapter 4 has been accepted for publication in Desalination and Water Treatment as: Higgins, C. J. & Duranceau, S. J. (2020). Modeling the mass transfer of 1,4-dioxane in a nanofiltration membrane process. Desalination & Water Treatment, 191, 1-10. Doi: 10.5004/dwt.2020.25890. Copyright permissions for the article can be found in APPENDIX A.
CHAPTER 2. LITERATURE REVIEW

This chapter highlights the pertinent existing literature related to the work conducted in this document. The literature review is demarcated into three major subsections: (i) overview of the NF process, (ii) overview of CECs and their removal from NF processes, and (iii) diffusion-based mass transfer modeling used to describe the behavior of CECs in a NF process.

Membrane Technologies for Potable Treatment

In drinking water treatment, pressure-driven membrane technologies are applied to remove contaminants from water by a driving force delivered across a semipermeable media (Howe et al., 2012). Pressure driven membranes can be described as microfiltration (MF), ultrafiltration (UF), NF, and RO, and are classified by solute exclusion size, or pore size, ranging from 0.1 micrometer (µm) to 0.0001 µm (Duranceau & Taylor, 2011). MF and UF remove particles via a sieving mechanism while NF and RO remove particles via a diffusion-controlled separation process (American Water Works Association, 2007). NF is often grouped with RO, and frequently referred to as “loose RO” or “membrane softening” as the technology requires less pressure and allows monovalent ions to pass through the membrane while removing divalent ions, color, and natural organic matter (NOM) from water (Hilal et al., 2004; Van der Bruggen, 2013).

Overview of Nanofiltration Membrane Process

NF membranes are commonly comprised of a thin, semipermeable synthetic polymer material consisting of polyamide (PA), cellulose acetate (CA), polypiperazine (PZ), or other poly-derivatives, with the most common being polyamide thin-film composite (PA-TFC) due to
superior separation performance and chlorine resistance (Wei et al., 2008; Yang et al., 2019).

Commercial NF membranes usually consist of a thin-layer composite manufactured as a stratified structure with a 100-200 nanometer (nm) thick PA “active” layer, a 50 µm polysulfone support layer, and a 200 µm polyester backing. The “active” layer is predominantly responsible for the rejection effectiveness of the membrane. NF membranes have a MWCO ranging from 200 Da (classified as tight) to 2,000 Da (classified as very loose) (Hilal et al., 2004). In potable water applications, the MWCO of NF allows removal of divalent ions and passage of monovalent ions. NF membranes can achieve 95 percent and 40 percent removal of divalent ions and monovalent ions, respectively (Mukiibi & Feathers, 2009). The primary application of NF in the drinking water industry is removal of hardness, color, NOM, and synthetic organic compounds from groundwater (Taylor et al., 1987; Duranceau et al., 1992; Gorenflo et al., 2003; Hilal et al., 2004). NF has recently gained traction in the Southeastern United States (US) as a water softening technology as much of the Upper Floridan Aquifer is classified as very hard (> 180 mg/L as CaCO3) (Rubenowitz-Lundin & Hiscock, 2012). However, NF processes can also be used for brackish water desalination and disinfection by-product control (Choi et al., 2001; Duranceau & Taylor, 2011; Howe et al., 2012).

In application, the thin-layer composite semipermeable flat-sheet is spirally wound and encased in a pressure vessel. Pressurized feed water travels across the membrane surface in an axial direction. Permeate flows radially to the center and exits through a collection tube. Concentrate does not pass through the membrane surface and is collected on the outer diameter of the membrane. To mathematically describe NF operation, a definitive boundary and mass balance approach is
utilized, shown in Figure 2-1. Equation 2-1 and 2-2 describe a flow and concentration mass balance around a membrane process. Example calculations are presented in APPENDIX B.

$$Q_F = Q_P + Q_C$$ \hspace{1cm} (2-1)

$$Q_F C_F = Q_P C_P + Q_C C_C$$ \hspace{1cm} (2-2)

Where,

$Q_F$ = feed water flow rate (gal/d)

$Q_P$ = permeate water flow rate (gal/d)

$Q_C$ = concentrate water flow rate (gal/d)

$C_F$ = feed water solute concentration (lb/ft$^3$)

$C_P$ = permeate water solute concentration (lb/ft$^3$)

$C_C$ = concentrate water solute concentration (lb/ft$^3$)
Recovery (R) is the ratio of permeate water to feed water and is calculated using Equation 2-3. Membrane processes can treat seawater and groundwater with elevated hardness levels at recoveries of 50 percent and 90 percent, respectively (Yonge et al., 2018). It is known that membrane processes encompass a direct relationship between recovery and permeate solute concentration. Membrane processes operating at high recoveries may experience fouling and performance decline due to accumulation of solute on the membrane surface, which forms due to concentration polarization (Crittenden et al., 2005). Rejection (r) describes the membranes ability to remove solute from water and is calculated using Equation 2-4.

$$R = \left(\frac{Q_P}{Q_F}\right) \times 100$$

(2-3)

$$r = \frac{C_F - C_P}{C_F} \times 100$$

(2-4)

Where,

$R =$ recovery (percent)

$r =$ rejection (percent)

Membrane operation can be described by the rate of solvent (water) and solute (contaminant) mass transfer. Water mass transfer is governed by net transmembrane pressure (NTP) and is described by Equations 2-5, 2-6, and 2-7. NTP is the pressure difference between the feed stream and permeate stream. The osmotic pressure ($\Delta \pi$) is the difference in potential energy between solutions on either side of a membrane surface (American Water Works Association, 2007). Typical feed pressures for a NF range from 50 to 200 pounds per square inch (psi) (Benjamin et al., 2002).
\[ NTP = \Delta P - \Delta \pi \]  
\[ \Delta P = \frac{1}{2} (P_F + P_C) - P_P \]  
\[ \Delta \pi = R_u \times \left[ \frac{1}{2} (C_F + C_C) \times T_F \right] - \left( C_P \times T_P \right) \]

Where,

\( NTP \) = net transmembrane pressure (psi)

\( \Delta P \) = transmembrane pressure differential (psi)

\( P_F \) = feed pressure (psi)

\( P_C \) = concentrate pressure (psi)

\( P_P \) = permeate pressure (psi)

\( \Delta \pi \) = transmembrane osmotic pressure (psi)

\( R_u \) = universal gas constant (1.206 L·psi/mol·K)

\( T_F \) = feed temperature (K)

\( T_P \) = permeate temperature (K)

Membrane operation is often monitored by flux, or the rate of transfer through a membrane surface (Duranceau et al., 1992). The flow of permeate per unit membrane area is known as water flux \((J_w)\) and is calculated using Equation 2-8. Water flux is a function of NTP and the water mass transfer coefficient (MTC) \((k_w)\). The water MTC is a distinct characteristic of the system, variant depending on water quality, membrane properties, and operating conditions (American Water Works Association, 2007). The flow of solute per unit membrane area is known as solute flux \((J_s)\)
and is calculated using Equation 2-9. Solute flux is a function of the concentration differential across the membrane and the solute MTC ($k_s$). The water MTC coefficient is based on convection, whereas the solute MTC is based on diffusion; however, both are in part dependent on the system’s properties. To achieve optimal treatment, a high water MTC and low solute MTC are desired.

$$J_w = k_w(\Delta P - \Delta \pi) = \frac{Q_P}{A} \tag{2-8}$$

$$J_s = k_s(C_M - C_P) = k_s \left( \frac{C_F + C_C}{2} - C_P \right) = \frac{Q_P C_P}{A} \tag{2-9}$$

Where,

$J_w =$ Water flux, (gal/ft²d)

$k_w =$ water mass transfer coefficient (gal/ft²d-psi)

$A =$ effective membrane area (ft²)

$J_s =$ Solute flux (lb/ft²d)

$k_s =$ solute mass transfer coefficient (ft/d)

$C_M =$ concentration of solute at membrane surface (lb/ft³)

**Overview of Chemicals of Emerging Concern**

Recently, regulation of drinking water treatment has been subject to become more stringent due to the introduction and detection of CECs in the environment through domestic, industrial, or commercial use (Murphy et al., 2012). The term CEC refers to unregulated chemicals used by
society including pharmaceuticals, personal care products, pesticides, industrial solvents, and flame retardants (Klecka et al., 2010). It is suspected that chronic exposure of trace concentrations of CECs may exhibit negative health effects on humans and other organisms (Nghiem et al., 2005; Kortenkamp et al., 2007; Snyder et al., 2007; Fawell & Ong, 2012; Raghav et al., 2013; Wang et al., 2018).

One of the principal portals in which CECs enter the environment is by means of wastewater effluent discharge, although other pathways may include poorly maintained sewers, septic tanks, landfills, and other disposal sites (Fawell & Ong, 2012). Most conventional wastewater treatment facilities are not intended to remove CECs, however some are degraded or removed in the biological treatment stage (Nghiem et al., 2005). It is important to note that CECs have most likely been released to the environment since their introduction to society, but the detection of lower levels through technological advancements and newfound public awareness has sparked interest and subsequent concern (Jones et al., 2006; Junior et al., 2016; Wee & Aris, 2019).

Concentrations of CECs can be found in wastewater effluent from ng/L to mg/L (Glassmeyer et al., 2016; Furlong et al., 2017). Consequently, due to the cyclic nature of the Earth, CECs have also been found in source water intended for potable purposes. For example, in a study conducted by the United States Environmental Protection Agency (USEPA), Glassmeyer and colleagues (2016) sampled source water from 25 independent water treatment facilities (WTFs) for 247 CECs and found 148 of the chemicals were detected at least once in source water, and 121 were detected at least once in treated drinking water. Such concerns have propelled research efforts in determining the existence, implications, transformation, and impacts of CECs on humans and other organisms (Fono & McDonald, 2008; Raghav et al., 2013).
The Safe Drinking Water Act (SDWA) requires the USEPA to quinquennially publish a list of CECs that may potentially pose risk in drinking water, known as the Candidate Contaminant List (CCL). The CCL serves as the basis for formal monitoring programs through the Unregulated Contaminant Monitoring Rule (UCMR) which provides support regarding the regulatory process of constituents in drinking water (Adamson et al., 2017). Therefore, the CCL and UCMR are primary sources of occurrence frequency and exposure data used to produce regulatory decisions for CECs.

Chemical of Emerging Concern Removal by Nanofiltration

Multiple research efforts have focused on evaluating the rejection capabilities of NF membranes for CECs. NF technology is known to remove some CECs, illustrated in Table 2-1. Much of the published research reports a range of rejection. It is known that the rejection of CECs by NF is contingent on a multitude of variables such as solvent (feed water), solute, membrane, and process properties, shown in Figure 2-2 (Darvishmanesh et al., 2010). The complexities of CEC mass transfer have been scrutinized and reported on over the years and serve as the basis for additional investigations such as those presented herein.
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Classification</th>
<th>Removal (percent)</th>
<th>Experimental configuration</th>
<th>Feed water matrix</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Dibromide</td>
<td>Insecticide</td>
<td>0</td>
<td></td>
<td></td>
<td>Duranceau et al. (1992)</td>
</tr>
<tr>
<td>Dibromochloropropane</td>
<td>Insecticide</td>
<td>35</td>
<td>Pilot-scale</td>
<td>Spiked groundwater</td>
<td></td>
</tr>
<tr>
<td>Chlordane</td>
<td>Insecticide</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptachlor</td>
<td>Insecticide</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>Insecticide</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alachlor</td>
<td>Herbicide</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td>Herbicide</td>
<td>10-42</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td>Devitt et al. (1998)</td>
</tr>
<tr>
<td>Estrone</td>
<td>Hormone</td>
<td>10-80</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td>Nghiem et al. (2004)</td>
</tr>
<tr>
<td>Estradiol</td>
<td>Hormone</td>
<td>20-90</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td>Kosutic et al. (2005)</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Solvent</td>
<td>36</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td></td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Analgesic</td>
<td>5-100</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td>Nghiem &amp; Hawkes (2007)</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Analgesic</td>
<td>30-100</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>Anti-epileptic</td>
<td>8-95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triclosan</td>
<td>Antimicrobial</td>
<td>82-90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>Antibiotic</td>
<td>0-60</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td>Yoon et al. (2007)</td>
</tr>
<tr>
<td>Iopromide</td>
<td>Radiopaque</td>
<td>0-70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>Analgesic</td>
<td>0-40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>Plasticizer</td>
<td>0-37</td>
<td>Bench-Scale</td>
<td>Spiked surface water, Membrane bioreactor effluent, synthetic water</td>
<td>Comerton et al. (2008)</td>
</tr>
<tr>
<td>Carbadox</td>
<td>Antibacterial</td>
<td>0-70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>Fibrate</td>
<td>0-92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>Analgesic</td>
<td>18-96</td>
<td>Bench-scale</td>
<td>Synthetic water</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Category</td>
<td>Concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-----------------</td>
<td>---------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>Stimulant</td>
<td>50-93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenazone</td>
<td>Analgesic</td>
<td>52-96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>Analgesic</td>
<td>75-99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Analgesic</td>
<td>75-99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17β Estradiol</td>
<td>Hormone</td>
<td>57-98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonylphenol</td>
<td>Surfactant</td>
<td>83-99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Solvent</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>Plasticizer</td>
<td>20-55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>Herbicide</td>
<td>88-92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>Analgesic</td>
<td>92-94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>Analgesic</td>
<td>85-90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentoxifylline</td>
<td>Analgesic</td>
<td>80-90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>Stimulant</td>
<td>65-70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>Anti-epileptic</td>
<td>85-90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEET</td>
<td>Insecticide</td>
<td>75-80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>Analgesic</td>
<td>85-90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Analgesic</td>
<td>78-85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluorooctane sulfonate</td>
<td>Fluorosurfactant</td>
<td>94-99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluconazole</td>
<td>Antifungal</td>
<td>97-100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metformin</td>
<td>Hypoglycemic</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Yangali-Quintanilla et al. (2009)

Bench-scale Spiked surface water, synthetic water

Sadmani et al. (2014)

Bench-scale Spiked surface water, synthetic water

Jeffery-Black & Duranceau (2016b)

Pilot-scale Spiked groundwater

Zhao et al. (2016)

Bench-scale Synthetic groundwater

Foureaux et al. (2019)

Bench-scale Spiked surface water
Influence of Solvent Properties on CEC Removal

Research has shown that the chemical makeup of feed-water compositions can influence CEC rejection. The pH of the feed water matrix influences the removal of charged CECs by changing the extent of electrostatic repulsion between the solute and membrane surface (Lin & Lee, 2014; Park & Snyder, 2020). Furthermore, feed water pH can also alter the charge if a CEC contains a log $K_a$ value (Ge et al., 2017). An increase in ionic strength has also been known to decrease CEC rejection by minimizing electrostatic repulsion between the solute and membrane surface (Devitt et al., 1998; Park & Snyder, 2020).

When compared to rejection in CEC-spiked deionized water (DI) solutions, rejection of chemicals in spiked natural and synthetic surface waters have been reported higher when organic-based compounds are present such as NOM (Devitt et al., 1998; Comerton et al., 2008; Sadmani et al., 2014; Foureaux et al., 2019). The presence of divalent ions in CEC-spiked DI and natural surface waters are also known to influence solute rejection, however findings are conflicting. Some have
reported a CEC rejection decrease when divalent ions such as calcium are present, as they ‘shield’ the membrane charge, leading to a decrease in electrostatic interactions between the solute and membrane surface, similar to the behavior of ionic strength (Verliefde et al., 2008). However, others have reported that divalent ions such as calcium and magnesium in synthetic groundwater improve CEC rejection by forming larger complexes, thus becoming rejected easier based on size (steric hinderance) (Zhao et al., 2013; Zhao et al., 2016). Divalent ions such as calcium have also been known to enhance the adsorption of CECs onto a membrane surface (Plakas et al., 2006). Such opposing results further the complexity of CEC rejection in naturally occurring water matrices.

Much of the published research involved using synthetic, or artificially created feed water with subsequent studies at the laboratory or bench-scale, shown in Table 2-1. Although some experiments have aimed at understanding CEC rejection in natural surface water matrices (Comerton et al., 2008; Sadmani et al., 2014; Foureaux et al., 2019), less research has been conducted regarding natural groundwater matrices (Jeffery-Black & Duranceau, 2016b).

**Influence of Process Properties on CEC Removal**

It is generally accepted that operating at higher recoveries yields lower CEC rejection (Chen et al., 2004). Operating pressure has also been known to affect CEC rejection. Higher operating pressure leads to a rise in permeate flux and subsequent increase in concentration polarization layer at the membrane surface, which corresponds to higher diffusion rates, yet since convection is the predominant transfer the quantity of permeate dilutes the solute concentration and hence higher rejection is realized. (Tang et al., 2007; Song et al., 2020). Operating NF membranes at high pressures can increase the amount of hydrophobic CEC adsorbed onto the membrane surface
Kimura et al., 2003a). Configuration of a membrane process can also affect rejection. For example, a two-pass NF process can increase CEC rejection (compared to a one-pass system). Conversely, the addition of concentrate recycle in a NF process can decrease CEC rejection (Zhu et al., 2009).

Influence of Solute Properties on CEC Removal

A strong research effort has attempted to elucidate the effect of CEC properties on solute rejection. It is widely accepted that molecular weight is an important parameter in the prediction of non-charged and non-polar compound removal (Ozaki & Li, 2002; Van der Bruggen & Vandecasteele, 2002; Schutte, 2003). However, other solute characteristics, such as chemical properties, geometry, and functional groups can also affect removal of CECs (Bellona et al., 2004; Yangali-Quintanilla et al., 2010). In a membrane process, correlations between CEC rejection and hydrophobicity (Comerton et al., 2008), membrane adsorption (Comerton et al., 2007), polarizability, molecular volume (Jeffery-Black & Duranceau, 2016b), polarity (Van der Bruggen et al., 1999; Darvishmanesh et al., 2011), molecular width, molecular mean size (Kiso et al., 2002), and molar length (Yangali-Quintanilla et al., 2010, Sadmani et al., 2014) have been noted. Recent literature has also reported that the position of functional groups in structural isomers can affect membrane rejection (Breitner et al., 2019).

Chirality

A solute property that has received little academic attention regarding behavior in a NF membrane process is chirality. Chirality is a geometric property that describes an isomers similarity. A key feature that discerns chirality in a molecule is the presence of an asymmetric carbon atom. Chiral molecules, or stereoisomers, are molecules with the same molecular formula and chemical bonding
arrangement, but different spatial arrangement of atoms. Enantiomers are pairs of stereoisomers that are non-superimposable mirror images. Enantiomers are termed under the designation ‘R’ or ‘S’, originating from the Latin words *rectus* and *sinister*, which mean “right”, and “left”, respectively (Cahn et al., 1966). Although enantiomers have the same molecular formula and other chemical properties, some are known to behave differently. For example, the R-enantiomer in chiral drug thalidomide (C13H10N2O4) has sedative effects, whereas the S-enantiomer is teratogenic (Franks et al., 2004).

Currently, there is little published research regarding the removal of chiral molecules through NF processes. Hence, the role of chirality in solute-membrane interactions in a NF process should be further investigated.

**Selected Solute in Research**

Ibuprofen and 1,4-dioxane were selected to extensively study interactions in a NF process. The solutes represent two classes of CECs: pharmaceuticals and industrial solvents. Both solutes have molecular weights in range of the NF MWCO, allowing the ability to investigate influence of solute concentration, feed-water matrix properties, and operational properties on rejection. The selected compounds have often been detected in raw supply sources and finished drinking waters, hence accentuating the need to elucidate rejection capabilities of existing treatment infrastructure such as NF (Adamson et al., 2014; Sui et al., 2015; Chen et al., 2019).

**Ibuprofen**

Ibuprofen ((RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid; IBU) is a weak propionic acid known for its non-steroidal anti-inflammatory (NSAID) properties. Ibuprofen is administered as
an over-the-counter medication commonly known as Advil® or Motrin®. The ibuprofen molecule contains a chiral carbon, yielding two enantiomers, S-ibuprofen and R-ibuprofen, as shown in Figure 2-3. Although medically administered ibuprofen is a racemic mixture of the two enantiomers, the S-form possesses most of the anti-inflammatory properties (Davies, 1998; Bonato et al., 2003). Like other pharmaceuticals, ibuprofen has been detected in wastewater effluents to the microgram per liter (µg/L) level (Sui et al., 2015; Jiménez-Silva et al., 2019). Although not considered harmful to humans, the existence of ibuprofen and other pharmaceuticals in the environment are of concern due to the possible adverse environmental impacts to aquatic and terrestrial ecosystems (Brozinski et al., 2012).

Chemical properties of ibuprofen are listed in Table 2-2. Due to its low Henry’s law constant (1.5×10^{-7} atm-m^3/mol), ibuprofen often persists in aquatic environments. However, ibuprofen’s moderately high octanol-water partition coefficient (log K_{ow}; 3.97) and soil organic carbon-water partition coefficient (log K_{oc}; 3.53) suggest moderate hydrophobicity, and therefore possible adsorptive qualities to clay and other loamy-solids. An acid dissociation constant (log K_a) of 4.4 yields a pH dependent speciation of ibuprofen, illustrated in Figure 2-4 and Equation 2-10.

![Figure 2-3: Ibuprofen enantiomers](image)
Table 2-2: Chemical properties of ibuprofen

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C_{13}H_{18}O_{2}</td>
</tr>
<tr>
<td>CAS No.</td>
<td>15687-27-1</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>206.28</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.03</td>
</tr>
<tr>
<td>Water solubility at 25°C (g/L)</td>
<td>0.021</td>
</tr>
<tr>
<td>Boiling point (°C at 760 mmHg)</td>
<td>157</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>76</td>
</tr>
<tr>
<td>Vapor pressure (mmHg at 25°C)</td>
<td>4.74×10^{-5}</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (log K\textsubscript{ow})</td>
<td>3.97</td>
</tr>
<tr>
<td>Soil organic carbon-water partition coefficient (log K\textsubscript{oc})</td>
<td>3.53</td>
</tr>
<tr>
<td>Henry’s law constant at 25°C (atm-m^3/mol)</td>
<td>1.5×10^{-7}</td>
</tr>
<tr>
<td>Acid dissociation constant (log K\textsubscript{a})</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Note: molecular weight, boiling point, melting point obtained from O’Neil (2001), water solubility obtained from Yalkowsky & Dannenfelser (1992), log K\textsubscript{ow} obtained from Avdeef et al., (1998), vapor pressure obtained from Daubert & Danner (1989), log K\textsubscript{a} obtained from Shaw et al., (2008), log K\textsubscript{oc} and Henry’s law constant obtained from EPI-Suite (2008)

Figure 2-4: Ibuprofen speciation based on log K\textsubscript{a} value (4.4)
\[ C_{12}H_{17}COOH + H_2O \leftrightarrow H_2O + C_{12}H_{17}COO^- + H^+ \] \hspace{1cm} \text{Log } K_a = 4.4 \hspace{1cm} (2-10)

Research has shown that ibuprofen rejection via NF is dependent on pH, membrane type, and other aforementioned factors presented in Figure 2-2 (Lin & Lee, 2014; Ge et al., 2017). However, the behavior of individual enantiomers of ibuprofen in a NF process has received little attention, and factors that may influence rejection such as solute concentration, feed-water matrix, and operating pressure could be investigated to gain further understanding of mass transfer.

1,4-Dioxane

The chemical 1,4-dioxane (1,4-dioxacyclohexane) is a heterocyclic organic CEC listed on the USEPA’s CCL4 and UCMR3. Typically, 1,4-dioxane is used as an industrial solvent in adhesives, textiles, cosmetics, and dyes, and exists as a by-product of soap, polyester, and plastics manufacturing (Abe 1999; Chen et al., 2019). Detection of 1,4-dioxane in groundwater ranges from undetected to 1,000 µg/L, and up to 100,000 µg/L at some contaminated groundwater sites (Adamson et al., 2014; Chen et al., 2019). The USEPA and International Agency for Research on Cancer has classified 1,4-dioxane as a Class B2 (probable) human carcinogen due to the increased prevalence of carcinomas in rats and guinea pigs when exposed chronically to the organic compound (National Cancer Institute, 1978; Zenker et al., 2003). Although currently unregulated, the USEPA has issued a health advisory level of 0.35 µg/L in potable water, and states within the US have set even more stringent notification levels and guidelines (Mohr, 2001; USEPA, 2010; Zhang et al., 2017; McElroy et al., 2019). Research from the USEPA’s UCMR3 suggests that 1,4-
dioxane has been frequently detected in US public water supplies, prompting the need to consider alternative treatment in response to future regulation (Adamson et al., 2017).

Properties of 1,4-dioxane are listed in Table 2-3, which highlight the mobility and persistence of the chemical in water. A low Henry’s law constant (4.8×10⁻⁶ atm-m³/mol) suggests that 1,4-dioxane tends to persist in aqueous environments. A low log Kₜₐₜ (0.27) and log K₉ₒ (0.54) indicates that 1,4-dioxane is hydrophilic and does not have significant adsorptive capabilities to soil (Stepien et al., 2014; Zhang et al., 2017). Hence, 1,4-dioxane is often difficult to remove from water and wastewater streams (Zenker et al., 2003).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₄H₈O₂</td>
</tr>
<tr>
<td>CAS No.</td>
<td>123-91-1</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>88.1</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>1.03</td>
</tr>
<tr>
<td>Water solubility at 25°C (g/L)</td>
<td>Miscible</td>
</tr>
<tr>
<td>Boiling point (°C at 760 mmHg)</td>
<td>101.1</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>11.8</td>
</tr>
<tr>
<td>Vapor pressure (mmHg at 25°C)</td>
<td>38.1</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (log Kₜₐₜ)</td>
<td>-0.27</td>
</tr>
<tr>
<td>Soil organic carbon-water partition coefficient (log K₉ₒ)</td>
<td>0.54</td>
</tr>
<tr>
<td>Henry’s law constant at 25°C (atm-m³/mol)</td>
<td>4.8×10⁻⁶</td>
</tr>
</tbody>
</table>

Note: molecular weight and water solubility obtained from Budavari et al., (1989); density obtained from Keith and Walters (1985), boiling point, melting point vapor pressure obtained from Verschueren, (1983), log Kₜₐₜ, log K₉ₒ, Henry’s law constant obtained from Howard (1990)
It is known that conventional water treatment processes are generally ineffective at rejecting 1,4-dioxane (Zenker et al., 2003; DiGuiseppi et al., 2016). However, adsorption through granular activated carbon, and biodegradation via advanced oxidative processes have shown moderate 1,4-dioxane removal success (Son et al., 2009; Chitra et al., 2012; Woodard et al., 2014). Research studying the rejection of 1,4-dioxane from NF and RO is in its infant stages. Kosutic et al. (2000) used 1,4-dioxane as a reference solute for pore size distribution of a HR95PP RO membrane, TFC-88821ULP RO membrane, and TS80 NF membrane, and found average rejections of 92 percent, 88 percent, and 81 percent, respectively. In a similar study conducted by Kosutic et al. (2005), rejection of 1,4-dioxane for a NF270 membrane was on average 36 percent. Yangali-Quintanilla et al. (2010) reported 1,4-dioxane rejection of 45 percent for a NF-90 membrane.

**Mass Transfer Modeling**

A better understanding of fundamental performance is needed for membrane processes to gain traction in treating municipal drinking water. Membrane models are essential to accurately describe process behavior to minimize risk in the design of a new process (Marriott & Sørensen, 2003; Zhao et al., 2005). Frequently used models to determine NF and RO membrane behavior consist of the Nernst-Planck equation, homogeneous solution diffusion model (HSDM), or non-linear regression (Schlögl, 1966; Spiegler & Kedem, 1966; Duranceau et al., 1992; Wijmans & Baker, 1995; Taylor & Jacobs, 1996; Jeffery-Black et al., 2017). The HSDM is a diffusion-based model used to predict permeate concentrations, and is dependent on water and solute MTCs, osmotic pressure differential, and NTP. The HSDM, shown as Equation 2-11, is derived by rearranging membrane mass balance equations (Equations 2-1 and 2-2), recovery (Equation 2-3), water flux (Equation 2-8), solute flux (Equation 2-9) and solving for permeate concentration ($C_p$).
The derivation of the HSDM is shown in APPENDIX B. The HSDM assumes that solute and solvent mass transfer is due to pressure and concentration gradients, respectively (Wijmans & Baker, 1995; Taylor et al., 2000; Zhao et al., 2005;).

\[
C_P = \frac{k_s C_F}{k_w (\Delta P - \Delta \pi) \left(\frac{2 - 2R}{2 - R}\right) + k_s} \tag{2-11}
\]

The HSDM model is reliant on solute flux (J_s) and solute MTC (k_s), which are controlled by diffusion. The solute MTC can be determined experimentally or empirically by applying Sherwood number correlation equations (Sherwood et al., 1967). The HSDM can be further expanded upon by incorporating film theory (FT), which includes effects from concentration polarization, and is known as the HSDM-FT, shown in Equation 2-12.

\[
C_P = \frac{k_s C_F \exp \left(\frac{J_w}{k_b}\right)}{k_w (\Delta P - \Delta \pi) \left(\frac{2 - 2R}{2 - R}\right) + k_s \exp \left(\frac{J_w}{k_b}\right)} \tag{2-12}
\]

\[
\frac{C_{FC} - C_P}{C_B - C_P} = \exp \left(\frac{J_w}{k_b}\right) \tag{2-13}
\]

Where,

- \(C_B\) = Solute concentration in the bulk solution (lb/ft^3)
- \(k_b\) = solute back-transport mass transfer coefficient (ft/d)

Concentration polarization occurs when increased concentrations of solute reside at the membrane-liquid interface. Convective transport brings solute and solvent to the membrane surface. As solvent passes through the membrane, an accumulation of solute occurs on the membrane surface,
creating a concentration gradient. This gradient allows diffusion-based mass transport to occur backwards toward the feed solution, and can be described as the solute back-transport MTC \((k_b)\) in the HSDM-FT.

The HSDM and HSDM-FT models assume a constant solute MTC but have incurred error due to the linear approximation of a feed concentration composition. Therefore, an integrated HSDM and HSDM-FT were created by Mulford et al., (1999), referred to as the IHSDM and IHSDM-FT, shown in Equations 2-14 and 2-15, respectively.

\[
C_P = \frac{k_s C_F}{-RJ_W \ln \left(1 - \frac{RJ_W}{J_W + k_s}\right)} \quad (2-14)
\]

\[
C_P = \frac{k_s C_F}{-RJ_W e^{J_W/k_b} \ln \left(1 - \frac{RJ_W}{J_W + k_s e^{J_W/k_b}}\right)} \quad (2-15)
\]

The models were further modified to consider changes in flux, pressure, and osmotic pressure through the membrane process, and are known as the Integrated Osmotic Pressure Model (IOPM) and Integrated Osmotic Pressure Model with Film Theory (IOPM-FT), displayed in Equations 2-16 and 2-17, respectively (Zhao & Taylor, 2005).

\[
C_P = \frac{C_F}{R} \left\{ 1 - \frac{\Delta P - k_{TDS} TDS_C}{\Delta P - k_{TDS} TDS_F (1 - R)} \frac{k_s}{k_w \Delta P + k_s} \right\} \quad (2-16)
\]

\[
C_P = \frac{C_F}{R} \left\{ 1 - \frac{\Delta P - k_{TDS} TDS_C}{\Delta P - k_{TDS} TDS_F (k_s + k_w \Delta P)} (1 - R) \frac{1 - \left[ \exp^{k_b} \right] k_w \Delta P}{k_w \Delta P + k_s} \right\} \quad (2-17)
\]

Where,
\( k_{\text{TDS}} = 0.01 \text{psi/(mg/L TDS)} \)

The determination of the solute MTC \((k_s)\) can either be conducted experimentally, or by applying a numerical method such as the Sherwood correlation method. Sherwood relationships are contingent on membrane process flow and physical characteristics (Howe et al., 2012).

The Sherwood number is presented as Equation 2-18, and is a function of the Reynolds number \((R_e)\) (assuming laminar flow), the Schmidt number \((S_c)\), hydraulic diameter \((d_h)\), and the membrane channel length \((L_m)\). Reynolds’ number is presented as Equation 2-19, and is a function of hydraulic diameter, feed channel velocity \((v)\), density of water \((\rho)\), and solution viscosity \((\mu)\).

Schmidt number is presented as Equation 2-20, and is a function of solution viscosity, density, and solute diffusivity \((D_i)\). Solute diffusivity is presented as Equation 2-21 and is a function of the solvent association factor \((\varphi)\), MW, temperature \((T)\), viscosity, and solute molar volume at boiling point \((V_i)\). The relationship between Sherwood number, solute diffusivity, and hydraulic diameter determines the solute MTC, shown in Equation 2-23. The proposed empirical notion is supported by many researchers in finding the solute MTC, which can then be used in the HSDM and HSDM-FT, or modifications of the models (Duranceau, et al., 1992; Jeffery-Black et al., 2017).

\[
S_h = 1.86 \left( R_e S_c \frac{d_h}{L_m} \right)^{0.33} \quad (2-18)
\]

\[
R_e = \frac{d_h v \rho}{\mu} \quad (2-19)
\]

\[
S_c = \frac{\mu}{\rho D_i} \quad (2-20)
\]

\[
D_i = \frac{(117.3 \times 10^{-18})[\varphi(MW)]^{0.5}(T)}{\mu V_i^{0.6}} \quad (2-21)
\]
\[ d_h = 4\left(\frac{xy}{2(x + y)}\right) \]  \hspace{1cm} (2-22)

\[ k_s = \frac{S_h D_l}{d_h} \]  \hspace{1cm} (2-23)

Where,

\( S_h \) = Sherwood number (dimensionless)

\( R_e \) = Reynolds number (dimensionless)

\( S_c \) = Schmidt number (dimensionless)

\( d_h \) = hydraulic diameter (ft)

\( L_m \) = membrane length (ft)

\( x \) = membrane channel width (ft)

\( y \) = membrane feed channel spacer height (ft)

\( v \) = feed channel velocity (ft/s)

\( \rho \) = density of water (997 kg/m\(^3\))

\( \mu \) = viscosity (9.325 \( \times \) \( 10^{-4} \) kg/m-s)

\( D_l \) = diffusivity of solute (m\(^2\)/s)

\( \varphi \) = solvent association factor (2.26)

\( MW \) = molecular weight of solvent (g/mole)

\( V_l \) = solute molar volume at normal boiling point (m\(^3\)/mol)
Diffusion-based models can be applied to any solute that primarily diffuses across a membrane surface. The models have been used in numerous membrane applications (Duranceau et al., 1992; Zhao et al., 2005; Hidalgo et al., 2013; Jeffery-Black et al., 2017). Duranceau and colleagues (1992) studied the removal of six synthetic organic compounds and modeled their mass transport by means of the HSDM. The research demonstrated that the experimental derived solute MTC was comparable to the same value calculated by dimensional analysis and Sherwood calculations. However, empirical calculations revealed a slightly smaller solute MTC, which could be due to inaccurate membrane dimensions or conservative Wilke-Chang theoretical diffusivity. Zhao & Taylor (2005) developed and verified a fully-integrated osmotic pressure model (IOPM) using RO data from multiple full and pilot-scale membrane plants. Results indicate that the IOPM improved predictability of permeate concentrations when compared to the HSDM.

Hidalgo and colleagues (2013) used the HSDM to model atrazine permeate concentrations of different NF and RO membranes, and found that the model was accurate for permeate streams that contained lower levels of the contaminant. Jeffery-Black and colleagues (2017) utilized the HSDM and HSDM-FT to model mass transport of caffeine through a NF membrane. Correlations of predicted verses actual caffeine concentrations were 0.99, 0.96, and 0.99 for the HSDM without FT, HSDM-FT, and the Sherwood number, respectively. The HSDM-FT over predicted caffeine concentrations by 27 percent. It would appear that research should continue to determine the predictability of diffusion-based models for newly discovered CECs present in aquatic systems.
CHAPTER 3. MATERIALS AND METHODS

This chapter highlights the equipment, experimental procedures, preparation etiquette, and data analysis techniques utilized in this work. This chapter is delineated into five major subsections: (i) bench-scale ibuprofen enantiomer experimental protocol, (ii) pilot-scale 1,4-dioxane experimental protocol, (iii) model implementation, (iv) general water quality parameters observed, and (v) laboratory quality control.

**Bench-Scale Ibuprofen Enantiomer Removal Experimental Protocol**

Bench-scale experiments are often used in research applications to investigate the mechanisms of a full-scale process’s operation. Bench-scale experiments offer a controlled environment where the means of an action can be studied without the impact of external factors. Bench-scale environments also provide the ability to examine the influence of numerous variables without hefty interludes. In this research, a bench-scale, flat-sheet NF process was utilized to ascertain the adsorption and rejection of ibuprofen enantiomers. The experimental setup, procedure, sample analysis, and data evaluation of the bench-scale ibuprofen enantiomer experiments are presented in this Chapter.

**Experimental Setup**

**NF Bench-Scale, Flat-Sheet Unit**

A bench-scale, flat-sheet membrane unit was constructed and housed at the UCF Water Quality Engineering Research laboratories (Orlando, FL, USA) and utilized in this work, illustrated in Figure 3-1. The unit consisted of a Wanner Engineering M-03S Hydra-Cell 1.8 gallon per minute
(gal/min) pump (Minneapolis, MN, USA) with a Control Techniques variable frequency drive (VFD) (Eden Prairie, MN, USA), a 19 liter (L) Sterlitech stainless-steel conical feed reservoir (Kent, WA, USA), two Sterlitech CF042 acrylic cells which housed the membrane coupons (operated in parallel for duplicity), and accompanying appurtenances such as flowmeters, pressure gauges, check valves, and stainless-steel braided hose. Two MyWeigh CTS-600 scales (Phoenix, AZ, USA) were implemented for permeate collection and water flux measurements.

In this research, two NF membranes were assessed: Dupont Filmtec NF270 (Edina, MN, USA) and Microdyn Nadir Trisep TS40 (Goleta, CA, USA). Membrane properties are listed in Table 3-1. The MWCO for both membranes are in the range of the molecular weight of ibuprofen (206.29 grams per mol; g/mol), therefore removal values of the chemical can be determined, and variation in rejection due to water matrix, solute concentration, or operational variables can be investigated.
### Table 3-1: NF membrane properties

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Membrane type</th>
<th>MWCO (Da)</th>
<th>MgSO₄ rejection (percent)</th>
<th>Maximum operating temperature (°C)</th>
<th>Maximum operating pressure (psi)</th>
<th>Operating pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>PA TFC</td>
<td>200 - 400</td>
<td>&gt; 97.0</td>
<td>45</td>
<td>600</td>
<td>2 - 11</td>
</tr>
<tr>
<td>TS40</td>
<td>PZ</td>
<td>200 - 300</td>
<td>&gt; 98.5</td>
<td>45</td>
<td>600</td>
<td>2 - 12</td>
</tr>
</tbody>
</table>

Note: values obtained by manufacturer

**Experimental Procedure**

The bench-scale, flat-sheet unit was operated by pumping feed water through two independent membrane coupons that each produced a permeate and concentrate stream. During each experiment, permeate and concentrate streams were recycled back into the feed reservoir to simulate a constant feed composition, illustrated in Figure 3-2. Permeate tubes were taken from the feed reservoir and collected when appropriate, shown in Figure 3-3. Volume of permeate collected over time was measured by a scale to determine water flux ($J_w$).

![Figure 3-2: Flat-sheet bench-scale unit schematic (recycle mode)](image-url)
Figure 3-3: Flat-sheet bench-scale unit schematic (permeate collection mode)

Feed flow was controlled with the VFD and set at 0.264 gal/min (1.0 liter per minute; L/min) corresponding to a crossflow velocity of 0.590 feet per second (ft/s) (0.18 meter per second; m/s). Feed pressure was controlled by the concentrate control valve. When applicable, a chiller-coil system was utilized to sustain a feed water temperature of 20 plus or minus (±) one degree Celsius (°C).

Membrane coupons were cut to the desired dimensions (6.51 square inches (in²) effective membrane area, 2.25 in × 4.5 in; 42 square centimeters; cm²) and immersed in DI water for at least 24 hours (h). In each experiment, two pre-wet membrane coupons of the same manufacturer were inserted into respective CF042 cells in the bench-scale, flat-sheet unit and compacted under pressure for at least 24 h with DI. After 24 h, the DI was flushed from the system, and replaced
with the desired feed water matrix spiked with a racemic concentration of ibuprofen. If desired, the feed water pH was adjusted by 1 M sodium hydroxide (NaOH) or 5.8 M hydrochloric acid (HCl). The bench-scale, flat-sheet unit was then repressurized with the experimental feed water matrix and operated for 24 h. Feed water samples were taken at 0 and 24 h, where permeate and concentrate aliquots were taken at 24 h. Concentrate samples were used to complete mass balance calculations, presented in APPENDIX D. The unit was flushed at least twice with 5 L of DI in between experiments.

At 24 h, the ibuprofen in the solution was assumed to be in quasi-equilibrium with any ibuprofen that may have adsorbed onto the surface of the equipment and membrane. However, a much longer term may be required to reach a realistic systematic thermodynamic equilibrium. Others have agreed that 24 h of operation was adequate for equilibration of hydrophobic compounds (Kimura et al., 2003b).

Experiments were conducted to determine NF rejection mechanisms of ibuprofen for two different NF membranes at various feed solute concentrations, feed water pH levels, operational pressures, and feed water matrices. Figure 3-4 lists the specific variables investigated, and Table 3-2 illustrates the parameters applied in each experiment. The rejection of ibuprofen was examined with NF270 and TS40 membranes for at least seven solute concentrations in the µg/L order of magnitude. Ibuprofen rejection was also investigated as a function of pH, from 4.0 to 6.0 units. The specific acidic pH range was selected due to the log $K_a$ of ibuprofen (4.4). Ibuprofen rejection was also examined as a function of groundwater matrix. A synthetic groundwater (SGW) consisting of calcium and sulfate and a natural groundwater (NGW) consisting of calcium, chloride, magnesium, NOM, sulfate, and other ions were utilized in this research. Experiments
were also performed at multiple feed water pressures (corresponding to variant solute and water flux) to determine if operational parameters influenced ibuprofen rejection.

In addition, experiments using the flat-sheet setup without a membrane coupon installed were conducted to determine possible ibuprofen loss due to volatilization or adsorption, shown in Figure 3-5. Detailed experiments illustrating each variable used is displayed in Table 3-3.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Solute concentration</th>
<th>Water matrix</th>
<th>Operational pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>• NF270</td>
<td>• 1-1,500 µg/L</td>
<td>• DI, pH 4.0&lt;br&gt;• DI pH 5.0&lt;br&gt;• DI, pH 6.0&lt;br&gt;• Synthetic groundwater, pH 5&lt;br&gt;• Town groundwater, pH 5</td>
<td>• 50 psi&lt;br&gt;• 100 psi&lt;br&gt;• 150 psi</td>
</tr>
<tr>
<td>• TS40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-4: Experimental variables studied for ibuprofen removal via NF process

<table>
<thead>
<tr>
<th>Solute concentration</th>
<th>Water matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 1-1000 µg/L</td>
<td>• DI, pH 3.0&lt;br&gt;• DI, pH 4.0&lt;br&gt;• DI, pH 5.0&lt;br&gt;• DI, pH 6.0&lt;br&gt;• DI, pH 7.0&lt;br&gt;• Synthetic groundwater, pH 5.0&lt;br&gt;• Town groundwater, pH 5</td>
</tr>
</tbody>
</table>

Figure 3-5: Experimental variables studied for ibuprofen mass balance with flat-sheet equipment
Table 3-2: Experimental summary of ibuprofen rejection in bench-scale NF process

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Membrane</th>
<th>Target ibuprofen concentration (µg/L)</th>
<th>Feed water pH</th>
<th>Feed pressure (psi)</th>
<th>Feed water matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NF270</td>
<td>10</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>2</td>
<td>NF270</td>
<td>50</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>3</td>
<td>NF270</td>
<td>100</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>4</td>
<td>NF270</td>
<td>200</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>5</td>
<td>NF270</td>
<td>500</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>6</td>
<td>NF270</td>
<td>750</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>7</td>
<td>NF270</td>
<td>1,000</td>
<td>4.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>8</td>
<td>NF270</td>
<td>1,000</td>
<td>5.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>9</td>
<td>NF270</td>
<td>1,000</td>
<td>6.0</td>
<td>50</td>
<td>DI</td>
</tr>
<tr>
<td>10</td>
<td>NF270</td>
<td>1,000</td>
<td>5.0</td>
<td>50</td>
<td>NGW</td>
</tr>
<tr>
<td>11</td>
<td>NF270</td>
<td>1,000</td>
<td>5.0</td>
<td>50</td>
<td>SGW</td>
</tr>
<tr>
<td>12</td>
<td>NF270</td>
<td>50</td>
<td>4.0</td>
<td>150</td>
<td>DI</td>
</tr>
<tr>
<td>13</td>
<td>NF270</td>
<td>200</td>
<td>4.0</td>
<td>150</td>
<td>DI</td>
</tr>
<tr>
<td>14</td>
<td>NF270</td>
<td>500</td>
<td>4.0</td>
<td>150</td>
<td>DI</td>
</tr>
<tr>
<td>15</td>
<td>NF270</td>
<td>1,000</td>
<td>4.0</td>
<td>150</td>
<td>DI</td>
</tr>
<tr>
<td>16</td>
<td>TS40</td>
<td>10</td>
<td>4.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>17</td>
<td>TS40</td>
<td>50</td>
<td>4.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>18</td>
<td>TS40</td>
<td>100</td>
<td>4.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>19</td>
<td>TS40</td>
<td>500</td>
<td>4.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>20</td>
<td>TS40</td>
<td>750</td>
<td>4.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>21</td>
<td>TS40</td>
<td>1,000</td>
<td>4.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>22</td>
<td>TS40</td>
<td>1,000</td>
<td>5.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>23</td>
<td>TS40</td>
<td>1,000</td>
<td>6.0</td>
<td>100</td>
<td>DI</td>
</tr>
<tr>
<td>24</td>
<td>TS40</td>
<td>1,000</td>
<td>5.0</td>
<td>100</td>
<td>NGW</td>
</tr>
<tr>
<td>25</td>
<td>TS40</td>
<td>1,000</td>
<td>5.0</td>
<td>100</td>
<td>SGW</td>
</tr>
</tbody>
</table>
Table 3-3: Experimental summary of ibuprofen mass balance with flat-sheet equipment

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Target ibuprofen concentration (µg/L)</th>
<th>Feed water pH</th>
<th>Feed water matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>4.0</td>
<td>DI</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>4.0</td>
<td>DI</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>4.0</td>
<td>DI</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>4.0</td>
<td>DI</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>4.0</td>
<td>DI</td>
</tr>
<tr>
<td>6</td>
<td>1500</td>
<td>4.0</td>
<td>DI</td>
</tr>
<tr>
<td>7</td>
<td>1500</td>
<td>3.0</td>
<td>DI</td>
</tr>
<tr>
<td>8</td>
<td>1500</td>
<td>5.0</td>
<td>DI</td>
</tr>
<tr>
<td>9</td>
<td>1500</td>
<td>6.0</td>
<td>DI</td>
</tr>
<tr>
<td>10</td>
<td>1500</td>
<td>7.0</td>
<td>DI</td>
</tr>
<tr>
<td>11</td>
<td>1500</td>
<td>5.0</td>
<td>NGW</td>
</tr>
</tbody>
</table>

Sample Analysis

Solid Phase Extraction

Samples were collected in 150 milliliter (mL) salinized amber bottles, stored in a 4°C refrigerator, and extracted within 48 h of sampling. A solid phase extraction (SPE) method based on Hashim & Kahn (2011) was utilized to extract and preconcentrate R- and S- ibuprofen enantiomers. Extractions were performed utilizing a Waters vacuum manifold and Waters Oasis® HLB 3 mL, 60 milligram (mg) cartridges (Milford, MA, USA), shown in Figure 3-6. Cartridges were conditioned by gravity with 3 mL acetonitrile, followed by 3 mL methanol, and 3 mL HPLC grade water. Samples were then loaded through the SPE cartridges under vacuum of approximately 4 pounds per square inch (psi) and a constant flow rate of less than 2 milliliters per minute (mL/min). Sample bottles were then washed with 6 mL of HPLC grade water, which was also sent through
the cartridges. Cartridges were then dried for 5 minutes (min) under a vacuum pressure of 10 psi, and then eluted into sample tubes by gravity with 4 mL acetonitrile. Samples were then evaporated using an Organomation N-EVAP® nitrogen gas evaporator with water bath at 65°C (Berlin, MA, USA), shown in Figure 3-6. Samples were then reconstituted with 1 mL methanol:formic acid (100:0.1 v/v), manually agitated to dissolve the residue, and inserted into 1 mL amber sample vials, shown in Figure 3-7 (right). Samples were analyzed within 7 days of extraction.

![Figure 3-6: A photograph of SPE in process (left) and Organomation N-EVAP® nitrogen gas evaporator (right)](image)

**High Performance Liquid Chromatography**

The R- and S- enantiomers of ibuprofen were analyzed via a Perkin-Elmer Series 200 high performance liquid chromatography (HPLC) instrument (Santa Clara, CA, USA). The instrument consisted of a Series 200 binary pump, Series 200 autosampler, Series 200 vacuum degasser, and a D-Star Instruments DWV-10 variable wavelength detector set at 230 nanometers (nm), illustrated in Figure 3-7 (left) (Manassas, VA, USA). Separations were carried out on a Chiral Technologies,
Inc. CHIRALCEL® OJ-H column (4.6 × 150 millimeter (mm), inner diameter, 5 micrometer (µm) particle size; West Chester, PA, USA). The column was operated in polar phase mode, with an isocratic mobile phase consisting of methanol: formic acid (100:0.1, v/v) at a flow rate of 1 mL/min. Sample run time was 5.0 min with a 10.0-µL injection volume. It was found that R-ibuprofen eluted at 2.26 min, and S-ibuprofen eluted at 2.47 min, as shown in the chromatograph pictured as Figure 3-8.

![Figure 3-7: A photograph of the Perkin Elmer HPLC (left) HPLC sample vials (right)](image)

![Figure 3-8: HPLC ibuprofen enantiomer chromatogram](image)

1: R-ibuprofen
2: S-ibuprofen
Contact Angle

A ramé-hart Model 100 goniometer (Succasunna, NJ, USA) was utilized to determine membrane hydrophobicity via contact angle. Contact angle measurements were attained utilizing the sessile drop technique (Kwok et al., 1997; Al-Amoudi et al., 2008). Membrane coupons were dried and inserted on the stage with the active layer facing up. A micrometer syringe delivered a droplet of DI water onto the membrane surface, and a contact angle was measured by the goniometer. To obtain a representative contact angle of the entire membrane surface, ten contact angle measurements were taken on various areas of the membrane coupon and averaged.

![Figure 3-9: A photograph of the ramé-hart goniometer](image)

Data Analysis

Both R- and S- ibuprofen standard curves were analyzed with samples using the HPLC. The ibuprofen concentration was related to the area under the HPLC chromatograph curve, in microvolt-seconds (µV-s). Both R- and S- ibuprofen standard curves are presented in Figure 3-10. The standard curve equation was then used to relate the area under the HPLC chromatograph curve
to the ibuprofen concentration, facilitated by Microsoft® Excel (Redmond, WA, USA). Ibuprofen concentrations were adjusted by the preconcentration factor (150). Duplicate and spike samples were analyzed when appropriate.

![Standard curves of R- (left) and S- ibuprofen (right)](image)

Figure 3-10: Standard curves of R- (left) and S- ibuprofen (right)

**Pilot-Scale 1,4-Dioxane Removal Experimental Protocol**

Although bench-scale environments offer advantages regarding control and compactness, trends realized in bench-scale may not accurately scale up to full-scale operation. In such situations, pilot-scale experiments may be more advantageous. However, pilot systems can be costlier and less available than flat-sheet systems. In this research, an existing pilot-scale NF process located at the Towns of Jupiter Water Utilities WTF (Town; Jupiter, FL, USA) was utilized to ascertain the
rejection of 1,4-dioxane. The experimental setup, procedure, and sample analysis of the pilot-scale 1,4-dioxane experiments are presented herein.

Experimental Setup

NF Pilot-Scale Unit

A NF pilot-scale unit located at the Town (Jupiter, FL) and commissioned in December of 2014 was employed in this research. The NF pilot unit was designed to simulate the existing full-scale membrane process in the Town’s facility. Figure 3-11 illustrates the Town’s NF process, and highlights the split-feed, center-port configuration that is unique to the facility, and dimensionally similar NF pilot unit. Feed water is pressurized and fed on both sides of the train and travels through three elements, where concentrate is collected in the middle and permeate is collected on the ends. The intermediate concentrate (interstage) follows the same flow regime as the first stage, where flow is routed to the ends and travels through three elements, and concentrate is collected in the center. Utilizing center-port pressure vessels, a NF train can be designed wherein a more optimal hydraulic system could be achieved. Through a reduction in hydraulic losses associated with higher numbers of membrane elements linked in series, membrane productivity or flux can be increased. This configuration requires a lower osmotic pressure difference across the membrane surface, which saves energy when compared to a traditional NF configuration.
Figure 3-11: Schematic of Town’s split-feed, center-port NF process

The NF pilot unit (shown in Figure 3-12) contains a pretreatment system comprised of cartridge filters, scale inhibitor addition, and sulfuric acid injection. Feed water enters the pilot unit at 267 gallons per minute (gal/min). The membrane array is 7:2, with seven pressure vessels housing six membranes each in the first stage of treatment and two pressure vessels housing six membranes each in the second stage, totaling 54 membranes. The membranes in the pilot are analogous to membranes used in the full-scale process (8 in. NF270; Dow Filmtec). The water recovery (R) of the NF pilot unit is 85 percent. The NF pilot unit and NF full-scale process exist in the same quarters, shown in Figure 3-13.
The NF pilot unit contains a water quality sampling panel, and supervisory control and data acquisition (SCADA) control system. Specifications regarding the NF pilot unit are presented in Table 3-4. It is important to note that the NF pilot was designed to be dimensionally analogous to that of the full-scale process, as the pilot unit houses the same membranes, and operates at the identical recovery and water flux as the full-scale NF process.

Figure 3-12: A photograph of the NF pilot unit

Figure 3-13: A photograph of the full-scale NF trains (left) and pilot-scale NF unit (right) (Photo by Duranceau, 2015)
Table 3-4: NF pilot unit operational parameters

<table>
<thead>
<tr>
<th>Item</th>
<th>Pilot-Scale Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane module</td>
<td>8 in. NF270 (DOW Filmtec)</td>
</tr>
<tr>
<td>Membrane material</td>
<td>PA TFC</td>
</tr>
<tr>
<td>MWCO (Da)</td>
<td>200-400</td>
</tr>
<tr>
<td>NaCl rejection (percent)</td>
<td>40-60</td>
</tr>
<tr>
<td>Zeta potential at neutral pH (mV)</td>
<td>-21.6</td>
</tr>
<tr>
<td>Number of membrane elements</td>
<td>54</td>
</tr>
<tr>
<td>Array</td>
<td>7:2</td>
</tr>
<tr>
<td>Recovery (percent)</td>
<td>85</td>
</tr>
<tr>
<td>Surface area per membrane (ft²)</td>
<td>400 (37.2 m²)</td>
</tr>
<tr>
<td>Feed capacity (gal/min)</td>
<td>267 (60,642 L/hr)</td>
</tr>
<tr>
<td>Production capacity (gal/min)</td>
<td>226 (51,330 L/hr)</td>
</tr>
<tr>
<td>Design water flux (gal/ft²d)</td>
<td>15.1 (25.6 L/m²hr)</td>
</tr>
<tr>
<td>Operating feed pressure (psi)</td>
<td>57 (3.93 bar)</td>
</tr>
</tbody>
</table>

Note: membrane material, MWCO, NaCl rejection, and zeta potential obtained from López-Muñoz et al., (2009)

Experimental Procedure

Although 1,4-dioxane can be found naturally in the Town’s source water ranging from non-detectable to 0.13 µg/L, a higher concentration was needed in the feed water to effectively determine solute mass transfer and rejection. The chemical 1,4-dioxane was purchased from Sigma Aldrich (St. Louis, MO, USA), and injected into a feed basin containing existing pre-treated feed water. The solution was then mixed and sequentially pumped into the NF pilot unit using a 25.6 gallon per hour (gal/h; 96.9 liter per hour; L/h) positive displacement pump. Based on previous transient response work conducted on the NF pilot unit (Jeffery-Black & Duranceau, 2016a), 1,4-dioxane was pumped into the feed stream for at least 15 min to equilibrate the system prior to sample collection from feed, permeate, and concentrate streams. The experiment was repeated
eight times for a range of feed 1,4-dioxane concentrations from 180 ng/L to 38,400 ng/L, shown in Table 3-5.

Table 3-5: Experimental summary of 1,4-dioxane removal from pilot-scale NF process

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Feed Concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
</tr>
<tr>
<td>2</td>
<td>760</td>
</tr>
<tr>
<td>3</td>
<td>890</td>
</tr>
<tr>
<td>4</td>
<td>6200</td>
</tr>
<tr>
<td>5</td>
<td>15,800</td>
</tr>
<tr>
<td>6</td>
<td>27,000</td>
</tr>
<tr>
<td>7</td>
<td>37,600</td>
</tr>
<tr>
<td>8</td>
<td>38,400</td>
</tr>
</tbody>
</table>

Samples were collected in 1-L amber bottles and preserved with sodium sulfite (Na₂SO₃) and sodium bisulfite (NaHSO₃). Samples were shipped on wet ice and analyzed by a commercial laboratory. 1,4-Dioxane was analyzed via EPA Method 522 with a method detection limit of 150 ng/L.

Model Implementation

The HSDM was applied to model the mass transfer of ibuprofen enantiomers and 1,4-dioxane. Water MTCs were determined experimentally, and solute MTCs were determined experimentally and empirically, then inserted into the variations of the HSDM, illustrated in Figure 3-14. Experimental and theoretical outputs were compared using relative percent difference (RPD), root mean square error (RMSE), and paired *t*-tests.
Laboratory and Field Quality Control

Sample collection and water quality evaluations were conducted in accordance with Standard Methods for the Examination of Water and Wastewater (Standard Methods) (Baird et al., 2017). The protocols and testing established the sampling, handling, transport, and analytical methodology requirements for the analysis conducted in this research. Table 3-6 presents the laboratory methods conducted in this research.
Table 3-6: List of methods and equipment for water quality analysis

<table>
<thead>
<tr>
<th>Test</th>
<th>Test location</th>
<th>Method</th>
<th>Equipment description</th>
<th>Method detection level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>UCF Laboratory</td>
<td>SM: 2320 B. Titration Method</td>
<td>Sulfuric Acid Burette Titration</td>
<td>5 mg/L as CaCO3</td>
</tr>
<tr>
<td>Calcium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>UCF Laboratory</td>
<td>SM: 3120 B. Inductively Coupled Plasma Method</td>
<td>Inductively Coupled Plasma Spectrometer – Optical Emission Spectroscopy Perkin Elmer Avio 200</td>
<td>0.01 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>UCF Laboratory</td>
<td>SM: 4110 B. Ion Chromatography; SM: 4500 B. Argentometric Method</td>
<td>Ion Chromatography - Dionex ICS-1100 with AS40 Automated Sampler</td>
<td>0.2 mg/L</td>
</tr>
<tr>
<td>Sulfate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color (True)</td>
<td>UCF Laboratory</td>
<td>SM: 2120 C. Spectrophotometric-Single-Wavelength Method</td>
<td>HACH DR 2700 Spectrophotometer</td>
<td>1 PtCo</td>
</tr>
<tr>
<td>Conductivity</td>
<td>UCF Laboratory</td>
<td>SM: 2510 B. Laboratory Method</td>
<td>Myron L Ultrameter 4P II</td>
<td>0.01 μS/cm</td>
</tr>
<tr>
<td>(R/S) Ibuprofen</td>
<td>UCF Laboratory</td>
<td>EPA Method 1694</td>
<td>Perkin Elmer Series 200 HPLC</td>
<td>500 ng/L</td>
</tr>
<tr>
<td>pH</td>
<td>UCF Laboratory</td>
<td>SM: 4500-H+ B. Electrometric Method</td>
<td>Oakton pH Tester 30; Accumet Research AR 60</td>
<td>0.01 pH units</td>
</tr>
<tr>
<td>Temperature</td>
<td>UCF Laboratory</td>
<td>SM: 2550 B. Laboratory and Field Methods</td>
<td>Oakton pH Tester 30; Accumet Research AR 60</td>
<td>0.01 °C</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS)</td>
<td>UCF Laboratory</td>
<td>SM: 2540 C. Total Dissolved Solids Dried at 180 °C</td>
<td>Myron L Ultrameter 4P II</td>
<td>4 mg/L</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt;</td>
<td>UCF Laboratory</td>
<td>SM: 5910 B. Ultraviolet Absorption Method</td>
<td>HACH DR 5000 Spectrophotometer</td>
<td>0.01 cm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Pace Analytical</td>
<td>EPA 522</td>
<td>Perkin Elmer GC/MS or equivalent</td>
<td>150 ng/L</td>
</tr>
</tbody>
</table>
Laboratory Quality Control

Laboratory quality control measures (Method 1020 B. Quality Control from Standard Methods) were utilized to produce reputable data. Reagents used for chemical analysis were at least analytical grade. Glassware used in the study was washed with laboratory grade detergent, rinsed with 1:1 HCl and cleansed with DI prior to collection. Equipment was thoroughly flushed with DI water in between experiments. Laboratory reagent blanks were also analyzed when necessary to evaluate contamination from solvents or glassware. Field blanks were also analyzed when appropriate to assess influences from sampling and storage procedures.

Accuracy

The accuracy of a sample set is determined by spike recovery experiments. A known concentration of an analyte was added to a sample to detect accuracy. Percent recovery is calculated using Equation 3-1. Generally, percent recovery is accepted within the range of 80 to 120 percent (Rice et al. 2012). In this study, every fifth sample was spiked to check accuracy.

\[
\text{Percent Recovery} = \left( \frac{C_{s+sp} - C_s}{C_{sp}} \right) \times 100
\]  

(3-1)

Where,

\(C_s\) = concentration of the sample (mg/L)

\(C_{s+sp}\) = concentration of spiked sample (mg/L)

\(C_{sp}\) = concentration of known spike added (mg/L)
For the ibuprofen work, percent recovery tests were conducted to determine the retention of ibuprofen in the SPE cartridges. SPE recovery is calculated using Equation 3-2 (Matuszewski et al., 2003).

\[
SPE\ Recovery = \frac{S_{pre}}{S_{post}} \times 100
\]  

(3-2)

Where,

\[S_{pre} = \text{extracted sample with analyte (mg/L)}\]

\[S_{post} = \text{extracted blank with analyte spiked in after reconstitution (mg/L)}\]

Percent recovery can be graphed and represented as an accuracy control chart to detect instrument or preparation accuracy. Upper control limits (UCL) and lower control limits (LCL) are ± three standard deviations, and are calculated using Equation 3-3. Upper warning limits (UWL) and lower warning limits (LWL) are plus or minus two standard deviations, are calculated using Equation 3-4.

\[
UCL/LCL = x_{ave} \pm 3s_t
\]  

(3-3)

\[
UWL/LWL = x_{ave} \pm 2s_t
\]  

(3-4)

Where,

\[x_{ave} = \text{average of percent recoveries}\]

\[s_t = \text{standard deviation of percent recoveries}\]
**Precision**

The precision of a sample set is determined by duplicates. A duplicate is the analysis of two independent samples prepared from one aliquot. Precision of a sample can be calculated by relative percent difference (RPD) or the industrial statistic (I-stat), shown in Equations 3-5 and 3-6, respectively. In this study, every fifth sample was duplicated to check sample collection, handling, and preparation techniques.

\[
RPD = \frac{|C_s - C_d|}{\frac{C_s + C_d}{2}} \times 100
\]  \hspace{1cm} (3-5)

\[
I-stat = \frac{|C_s - C_d|}{\frac{C_s + C_d}{2}}
\]  \hspace{1cm} (3-6)

Where,

\( C_s \) = sample concentration (mg/L)

\( C_d \) = duplicate sample concentration (mg/L)

RPD or I-stat can be graphed and represented as a precision control chart to detect discrepancies in sample preparation procedure. The UWL and UCL were calculated in accordance with Equations 3-3 and 3-4. The developed precision and accuracy control charts for this research can be found in APPENDIX E.
CHAPTER 4. RESULTS AND DISCUSSION

This chapter offers the results of experiments carried out to determine removal capabilities, decipher rejection mechanisms, and assess model viability of two CECs: racemic ibuprofen and 1,4-dioxane. This chapter is organized into two key subsections, including (i) the results of the bench-scale ibuprofen enantiomer investigation and (ii) the pilot-scale 1,4-dioxane assessment.

Bench-Scale Ibuprofen Enantiomer Removal Experiments

Adsorption of Ibuprofen onto Flat-Sheet Equipment

Adequate mass balance tests are recommended in membrane filtration experiments to confirm that rejection is not affected by solute behavior such as volatilization, adsorption to material other than the membrane surface, or a reaction with the feed water matrix. Prior to the series of pressurized filtration tests, a mass balance confirmation experiment was conducted by circulating a 10 L feed solution containing 100 µg/L ibuprofen at a feed water pH of 4.0 units for 24 h through the flat-sheet equipment without a membrane coupon. Feed samples were taken at 0 and 24 h to determine the loss of ibuprofen, if any. After analysis, 23 percent loss of ibuprofen was observed during the experiment. Due to the low Henry’s law constant ($1.5 \times 10^{-7}$ atm-m$^3$/mol), volatilization was discredited as an explanation for the ibuprofen loss. In acidic conditions, ibuprofen is known to adsorb onto metal surfaces, and can protect metal from corrosion (Bhadra et al., 2017; Fajobi et al., 2019; Tasić et al., 2019). Additionally, ibuprofen is postulated to adsorb onto chromium-based metal-organic frameworks (Bueno-Perez et al., 2014). The stainless-steel material that comprises much of the flat-sheet equipment is composed of 16 percent chromium, 10 percent nickel, 2 percent molybdenum, and less than (<) 0.02 percent carbon (Davalos Monteiro et al., 2019). Therefore,
existing literature combined with physiochemical properties suggest ibuprofen adsorption onto the metal portion of the flat-sheet equipment (comprised of the reservoir, tubing, and chiller coil). Similar results have been realized with 9-anthracenecarboxylic acid adsorption onto NF flat-sheet equipment (Kimura et al., 2003a; Kimura et al., 2003b).

**Effect of Feed Concentration on Enantiomeric Ibuprofen Adsorption**

The extent of total ibuprofen adsorption onto the flat-sheet equipment was investigated by repeating the experiment six times for a total solute concentration span of 100 µg/L to 1.5 mg/L (R- and S- enantiomer range of 50 µg/L to 750 µg/L). Feed samples were collected at 0 and 24 h. Triplicate feed concentration measurements were taken and averaged.

Figure 4-1 illustrates the results of the flat-sheet equipment adsorption experiments, where the total ibuprofen adsorbed concentration is presented as a function of the initial solute content. In these experiments, R-ibuprofen is illustrated in the pink dots and S-ibuprofen is depicted in the blue stripes. Chiral selectivity ($SS/R$) is shown in the black diamonds and was determined as a ratio of the amount of adsorption of S-ibuprofen to R-ibuprofen. Error bars represent minimum and maximum values from triplicate analysis.
Data in Figure 4-1 indicates that the adsorption of ibuprofen increases with initial feed concentration, which lies in agreement with prior ibuprofen-metal adsorption studies (Tasić et al., 2019). It also appears that the adsorbed ibuprofen concentration may approach a saturated equilibrium in due course and can hence be modeled by adsorption isotherms.

There is an apparent difference between the adsorption of R- and S-ibuprofen onto the metal surface. At an initial total ibuprofen concentration of 100 µg/L, S-ibuprofen adsorbs 4.82 times more than R-ibuprofen. The ratio falls to 2.25 at an initial total ibuprofen concentration of 1.5 mg/L. Figure 4-2 illustrates a direct relationship between the amount of R- and S- ibuprofen adsorbed onto the metal surface. The associated linear equation can be used to predict the adsorption capabilities of one enantiomer of ibuprofen if the attachment behavior of its counterpart is known.
Although current literature on the adsorption behavior of enantiomers is scarce, some have claimed that ibuprofen can enantioselectivity adsorb onto chromium- and vanadium-based metal-organic frameworks (Bueno-Perez et al., 2014). Additionally, the S-enantiomer of ibuprofen has been seen to adsorb up to 10 times more than the R-enantiomer on a liposome membrane (Okamoto et al., 2016). In liposomes, enantioselectivity was ascribed to hydrogen bonding or hydrophobic interactions between the asymmetric carbons of the chiral molecule and the liposome. It is also known that the S-ibuprofen is far more capable of inhibiting cyclooxygenase (COX; an enzyme required for the synthesis of prostaglandins, which cause inflammation in the human body) than its R- counterpart (Evans, 2001). In COX-1 and COX-2, S-ibuprofen forms an ion pair with enzyme Arg-120 and a hydrogen bond with enzyme Tyr-355, shown in Figure 4-3 (Blobaum & Marnett, 2007). However, as Tyr-355 mutates (i.e. reduction of side chain) in COX-1, the ability of the enzyme to enantiomerically select S-ibuprofen is diminished (Orlando et al., 2014).
It is known that hydroxide ions from water can adsorb onto 316 stainless-steel, yielding a negatively charged surface (Tanaka et al., 2008). The mechanism of ibuprofen adsorption onto metal surfaces was postulated to be hydrogen bonding between the hydrogen on the carboxylate functional group of the solute and the oxygen on the metal surface (Seo et al., 2016). The weak bonds between ibuprofen and the metal surface were assumed to be removed when the equipment was flushed with DI in between experiments. Therefore, each individual experiment could yield a true adsorptive value for the associated initial feed concentration. Figure 4-3 depicts a comparison between the hydrogen bond formation of S-ibuprofen in the human body (left) and the adsorption of the enantiomer onto a stainless-steel metal surface (right).

Figure 4-3: S-ibuprofen bound to COX-2 (Orlando et al., 2014) (left); S-ibuprofen bound to stainless-steel surface (right)

A possible explanation for the disparate enantiomer behavior could reside in optimized molecular geometry between R- and S-ibuprofen. Studies have shown that when immersed in a racemic mixture, D-alanine preferentially adsorbed onto copper, nickel, and zinc (Seshadri et al., 2013). This may be due to difference in molar volumes of the optimized geometries derived using density
functional theory (DFT) computations. The DFT calculated molecular volume of D-alanine was 18.4 cubic centimeters per mole (cm$^3$/mol) smaller than L-alanine, which yielded a less-stalled approach to the metal surface than its L-counterpart (Seshadri et al., 2013).

DFT calculations are accepted as powerful theoretical methods that can determine geometric and chemical properties of organic interactions by representing the electrical potential by the electron density instead of orbitals (Wu et al., 2019). Additional theory of DFT is reported elsewhere (Tsuneda, 2014). In conjunction with experimental studies, DFT computations are integral to determining the different adsorption behavior of enantiomers on several surfaces. The DFT framework in this work used the gradient correction non-local correlation functional of Lee, Yang, and Parr (B3LYP) with a basis set of 6-31G*, using the online GAMESS software (Lee et al., 1988; Perri & Weber, 2014). Table 4-1 presents a comparison of the DFT derived total energies and geometric properties of R- and S- ibuprofen, and Figure 4-4 illustrates the dipole moment (depicted as an orange arrow) of the two enantiomers.

Table 4-1: DFT calculated energy and geometries of R- and S- ibuprofen

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Energy (Hartrees)</th>
<th>Surface area (Å$^2$)</th>
<th>Molecular volume (Å$^3$)</th>
<th>Dipole moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-ibuprofen</td>
<td>B3LYP/6-31G*</td>
<td>-656.3</td>
<td>179.5</td>
<td>199.3</td>
<td>2.018</td>
</tr>
<tr>
<td>S-ibuprofen</td>
<td>B3LYP/6-31G*</td>
<td>-656.3</td>
<td>173.1</td>
<td>194.3</td>
<td>5.404</td>
</tr>
</tbody>
</table>
Results indicate that the energies of R- and S- ibuprofen are approximately equal, however the surface area, volume, and dipole moment differ, which align with findings presented elsewhere (Raschi et al., 2015). R-ibuprofen exhibits a surface area and molecular volume 6.40 Å³ and 5.00 Å² larger than S-ibuprofen, respectively. Therefore, R-ibuprofen is bulkier than S-ibuprofen, rendering a more hindered approach to the surface of the solid. The tabulation and direction of dipole moments also varies between the two enantiomers, yielding 2.02 and 5.40 Debeye (1 Debeye = 3.336×10⁻³⁰ coulomb-meter) for R- and S- ibuprofen, respectively. The larger dipole moment of S-ibuprofen alludes to a higher stability when compared to the R- enantiomer. Moreover, solutes with dipole moments larger than water (1.85 Debeye) can possess increased interaction with surfaces in fluids (Tasić et al., 2019), which was realized in the results. It should be noted that the ratio of the S- to R- ibuprofen dipole moment (2.68) compares well with the S-ibuprofen adsorption selectivity at initial racemic ibuprofen concentrations greater than 300 µg/L (2.46). These findings provide a plausible explanation regarding the atypical behavior of chiral enantiomers in an aqueous environment.
Effect of Feed pH on Enantiomeric Ibuprofen Adsorption

The effect of pH on ibuprofen adsorption to flat-sheet equipment was investigated by altering the feed water pH to 3.0, 4.0, 5.0, 6.0, or 7.0 units with an initial racemic ibuprofen content of 1.5 mg/L (R- and S- enantiomer concentrations of 750 µg/L). Feed samples were collected at 0 and 24 h. Triplicate feed concentration measurements were taken and averaged. Figure 4-5 illustrates the results of the flat-sheet equipment adsorption experiments, where the total ibuprofen concentration adsorbed is presented as a function of the feed water pH. Error bars represent minimum and maximum values from triplicate analysis.

![Figure 4-5: R- and S- ibuprofen adsorption onto flat-sheet equipment as a function of pH](image)

The largest concentration of ibuprofen adsorbed occurred at a feed water pH 3.0 units, and subsequently displayed an inverse relationship with pH. This behavior occurred as a result of ibuprofen’s log $K_a$ value (4.4). At a feed water pH less than 4.4 units, ibuprofen gains a hydrogen
ion and becomes neutral. The hydrogen from neutral ibuprofen can bind with the oxygen from the hydroxide group on the surface of the stainless-steel. However, at a feed water pH greater than 4.4 units, ibuprofen loses a hydrogen and becomes anionic, thus diminishing its ability to efficiently adsorb onto the stainless-steel surface.

The selectivity of S-ibuprofen was over 3.0 at a feed water pH of 3.0 units and increased as pH was elevated. At a feed water pH of 6.0 and 7.0 units, less than 1.0 µg/L of R-ibuprofen was adsorbed, leading to a stark increase in selectivity in favor of the S- enantiomer. The apparent adsorption of ibuprofen onto metal surfaces is an important discovery that should be considered when collecting removal data from membrane processes. If adequate time is not allowed for adsorption of hydrophobic neutral CECs, inaccurate rejection values may be reported.

Adsorption of Enantiomeric Ibuprofen onto Flat-Sheet Equipment and Membrane in Operation

Determination of Membrane Operational Characteristics

Prior to pressurized ibuprofen enantiomer removal experiments, effective membrane properties were determined. Pure water flux of the NF270 and TS40 membranes were determined using DI water as a solvent, shown in Figure 4-6. The experiments were conducted at pressures from 25-200 psi, which satisfied the typical NF pressure range in application (Benjamin et al., 2002). Both membranes demonstrated a linear water flux relationship with a coefficient of determination (R²) greater than 0.989. The NF270 yielded a larger pure water flux coefficient (0.460 gallon per square foot day; gal/ft²d) than the TS40 (0.231 gal/ft²d), illustrated in Table 3-1. The higher pure water flux in the NF270 was attributed to the larger MWCO. Therefore, due to the greater pore size, additional feed water can travel through the NF270 membrane, yielding decreased pressure
requirements and rejection rate of solute. For the purpose of comparable water flux values, experiments utilizing the NF270 and TS40 membranes were operated at feed pressures of 50 and 100 psi, respectively.

![Graph showing membrane pure water flux as a function of applied pressure (psi)](image)

**Figure 4-6: Membrane pure water flux as a function of applied pressure (psi)**

Additional membrane properties are illustrated in Table 4-2. Virgin membrane contact angle was determined upon receipt of the membranes, and compacted membrane contact angle was determined after compaction with DI for 24 h followed by drying for at least 48 h. The NF270 and TS40 membranes are classified as hydrophilic, as the contact angle is less than 90 degrees (°). However, after pressurized contact with DI for 24 h, contact angle revealed a more hydrophobic membrane surface.
Table 4-2: NF membrane flat-sheet operational properties

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water flux coefficient (Lp)</th>
<th>Contact angle (virgin, °)</th>
<th>Contact angle (compacted, °)</th>
<th>Zeta potential (pH 4, mV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF270</td>
<td>0.460</td>
<td>30.6 ± 5.81</td>
<td>50.2 ± 6.11</td>
<td>-24</td>
</tr>
<tr>
<td>TS40</td>
<td>0.231</td>
<td>28.7 ± 4.93</td>
<td>43.3 ± 3.72</td>
<td>-26</td>
</tr>
</tbody>
</table>

*Obtained from Wadekar & Vidic, 2017

Adsorption of Enantiomeric Ibuprofen onto Flat-Sheet Equipment and Membrane in Operation

Although significant adsorption was observed onto the membrane equipment, ibuprofen has also been known to adsorb onto membrane surfaces at pH values less than its log $K_a$ (Lin & Lee, 2014). Therefore, an initial experiment was conducted to determine the adsorption of ibuprofen onto equipment and membrane components while in operation. A 10 L feed solution containing 100 µg/L racemic ibuprofen at feed water pH of 4.0 units was pressurized and circulated for 24 h through the flat-sheet equipment with membrane coupons inserted. Feed samples were taken at 0 and 24 h to determine the loss of ibuprofen. After analysis, 25 and 28 percent loss of ibuprofen were observed during the NF270 and TS40 experiments respectively, which suggested adsorption onto the membrane surfaces in addition to the stainless-steel equipment. Similar findings have been reported by others (Simon et al., 2009; Lin & Lee, 2014; Ge et al., 2017).
Effect of Feed Concentration on Enantiomeric Ibuprofen Adsorption

The extent of total ibuprofen adsorption onto the flat-sheet equipment and membrane in operation was investigated by repeating the experiment six times for a total solute concentration span of 75 µg/L to 1.08 mg/L (R- and S- enantiomer range of 35 µg/L to 540 µg/L). Feed samples were collected at 0 and 24 h. Triplicate feed concentration measurements were taken and averaged.

Figure 4-7 illustrates the results of the flat-sheet equipment and membrane coupon adsorption experiments, where the total ibuprofen concentration adsorbed is presented as a function of the total initial feed concentration. Operation with the NF270 and TS40 membranes are pictured left and right, respectively. Error bars represent minimum and maximum values from triplicate analysis.

Figure 4-7: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 membrane (left) and TS40 membrane (right) in operation (pH 4, water flux 25 gal/ft²d, temperature 20±1°C)
Analogous to Figure 4-1, Figure 4-7 illustrates increased ibuprofen adsorption as the initial concentration was elevated, and similar maximum adsorption equilibria and selectivity of S-ibuprofen adsorption. However, the amount of R- and S-ibuprofen adsorption yielded an additional 19.6 and 39.2 percent for the pressurized NF270 and TS40 membrane experiments, respectively, than equipment sorption alone. These results indicate supplementary ibuprofen adsorption, presumably onto the membrane surface. Hydrophobicity measurements on each membrane coupon further verified the additional adsorption of ibuprofen to the membrane surface.

At an initial racemic concentration of 1.08 mg/L, 83.7 µg/L ibuprofen adsorbed onto the equipment and NF270 membrane. On the contrary, at an initial racemic concentration of 840 µg/L, 93.6 µg/L ibuprofen adsorbed onto the equipment and TS40 membrane. Therefore, the TS40 membrane contained a slightly higher capacity to adsorb ibuprofen than the NF270 membrane. The difference of adsorption cannot be explained by pore size or surface hydrophobicity. Although the NF270 membrane was more hydrophobic and contained a larger pore size, it did not adsorb as much ibuprofen as the TS40 membrane. Others have postulated similar findings (Zhao et al., 2017). However, a possible explanation could reside in the thickness of the active layer of the membrane, or the affinity of the material to form hydrogen bonds with ibuprofen.

It should be noted that static batch experiments on the ibuprofen adsorptive capabilities of the membrane coupons have been conducted elsewhere (Lin & Lee, 2014). Batch adsorption experiments often do not represent actual adsorptive capabilities of membrane while in pressurized operation, and thus were not included in the research reported herein (Kimura et al., 2003a).
Effect of Feed Pressure on Enantiomeric Ibuprofen Adsorption

The effect of pressure on ibuprofen adsorption to flat-sheet equipment and membrane surface in pressurized operation was investigated by altering the feed pressure to 150 psi with an initial racemic concentration of approximately 1.5 mg/L (R- and S- enantiomer content of 750 µg/L). Feed samples were collected at 0 and 24 h. Triplicate feed concentration measurements were taken and averaged. Figure 4-8 presents the results of the ibuprofen adsorption experiments with the NF270 membrane at feed water pressures of 50 and 150 psi. Error bars represent minimum and maximum values from triplicate analysis.

![Figure 4-8: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 membrane at 50 and 150 psi feed pressure](image)

From Figure 4-8, a 173 percent increase of ibuprofen adsorption was noted when operating for 24 h from 50 psi to 150 psi. It was assumed that the additional adsorption was primarily onto the membrane surface, as the active layer was exposed to the increased pressure. The main sources of stainless-steel in the flat-sheet equipment (reservoir and chiller coil) did not endure significant
pressure changes as the reservoir was exposed to atmospheric pressure in both scenarios. However, some additional adsorption could have occurred in the stainless-steel piping that also experienced increased feed pressure. Increased adsorption onto the membrane coupon was verified by an additional increase of contact angle compared to lower pressure experiments.

The selectivity of S-ibuprofen decreased at a higher feed pressure, indicating that the increased driving force may propel additional R-ibuprofen onto the membrane surface despite its lower dipole moment. A conceivable explanation for the increased adsorption with pressure is that additional drag force allows ibuprofen to access more surface sites on the membrane surface. This hypothesis has been examined in existing literature by comparing the extracted portion of solute from a membrane in a batch and pressurized filtration test. Findings included that a greater portion of solute could not be extracted in the membrane in pressurized operation (Kimura et al., 2003a). Therefore, increased pressure may drive additional ibuprofen adsorption onto micropores on the membrane surface.

Adsorption increase onto membrane surface as a function of pressure has also been reported for other CECs such as naphthol, estrone, diuron, and estrogen (Kimura et al., 2003a; Nghiem et al., 2004; Wang et al., 2010; Semião & Schäfer, 2011). For example, the total adsorbed concentration of estrone and 17-β-estradiol doubled when feed pressure increased from 3 to 17 bar (43.5 psi to 246 psi) (Semião & Schäfer, 2011). Additional research should investigate the kinetics of ibuprofen adsorption at lower operating pressures. As membrane processes are dynamic, 24 h may not be enough time to equilibrate a membrane process treating water matrices composed with hydrophobic CECs. Based on this information, it would be important to determine if lower feed pressure operation can eventually drive the solute into the membrane pores that were easily
accessed at the higher feed pressure. However, fluctuations in feed concentration can enable a constant state of adsorption-desorption, further complicating the process of CEC attachment mechanisms onto membrane surfaces in operation (McCallum et al., 2008).

The extent of total ibuprofen adsorption onto the flat-sheet equipment and membrane while operating at elevated pressure was investigated by repeating the experiment three times for a total racemic concentration span of 325 µg/L to 1.87 mg/L (R- and S- enantiomer range of 162 µg/L to 935 µg/L). Feed samples were collected at 0 and 24 h. Triplicate feed concentration measurements were taken and averaged.

Figure 4-9 presents the results of the flat-sheet equipment and NF270 membrane coupon adsorption experiments, where the adsorbed ibuprofen content is presented as a function of the total initial ibuprofen concentration. Error bars represent minimum and maximum values from triplicate analysis.

![Figure 4-9: Adsorbed R- and S- ibuprofen onto flat-sheet equipment and NF270 (pH 4, water flux 70 gal/ft²d, temperature 20±1°C)](image-url)
In a similar fashion to Figure 4-7, Figure 4-9 illustrates increased ibuprofen adsorption with initial feed concentration. Moreover, adsorbed ibuprofen concentration may reach eventual saturation, and can thus be modeled by adsorption isotherms. It is noted that a 150 psi feed pressure resulted in an average of 2.72 times more ibuprofen adsorption than at 50 psi, yielding a pseudo-linear relationship between the applied force and the amount of solute adsorbed. Selectivity of S-ibuprofen slightly decreased as concentration increased, indicating an intensification of R-ibuprofen adsorption with feed content. Hydrophobicity measurements on each membrane coupon further verified the additional adsorption of ibuprofen to the membrane surface.

**Effect of Feed pH on Enantiomeric Ibuprofen Adsorption**

The effect of pH on ibuprofen adsorption to flat-sheet equipment and membrane components was investigated. In these experiments, the feed pH was adjusted to 4.0, 5.0, or 6.0 units with an initial racemic ibuprofen concentration of 1.5 mg/L (R- and S- enantiomer content of 750 µg/L). Feed samples were collected at 0 and 24 h. Triplicate feed concentration measurements were taken and averaged.

Figure 4-10 illustrates the results of the flat-sheet equipment and membrane coupon experiments, where the total ibuprofen concentration adsorbed is presented as a function of the feed water pH. Operation with the NF270 and TS40 membranes are pictured left and right, respectively. Error bars represent minimum and maximum values from triplicate analysis. Aligning with Figure 4-5, Figure 4-10 illustrates an indirect relationship between ibuprofen adsorption and pH, ascribed to ibuprofen’s log $K_a$ value (4.4). A similar increasing trend in S-ibuprofen selectivity was also realized.
At a feed pH of 4.0, 5.0, and 6.0 units, a respective 7.15, 3.76, and 9.79 percent increase of ibuprofen adsorption was noted for the equipment and membrane components. This further confirms the ability of the membrane surface to facilitate ibuprofen adsorption. Moreover, the TS40 exhibited a greater adsorption capacity at the pH values examined, suggesting higher adsorption capacity compared to the NF270 coupon.

**Impact of Enantiomeric Ibuprofen Adsorption on Membrane Hydrophobicity**

Ibuprofen adsorption onto the membrane surface was validated by an increase in membrane contact angle, under the premise that a hydrophobic solute attached onto a hydrophilic exterior drives the surface to be more hydrophobic. Membrane contact angle was found to have a positive direct relationship with the concentration of ibuprofen adsorbed. Figure 4-11 exhibits the increase in NF270 and TS40 contact angle (and hence hydrophobicity) as a function of adsorbed ibuprofen.
concentration onto the flat-sheet equipment and membrane components. Error bars represent one standard deviation of uncertainty. Contact angle snapshots in Figure 4-11 provide visual images of the linear increase in hydrophobicity with adsorbed ibuprofen concentration. Attachment mechanisms affecting the membrane surface include both hydrophobic interactions and the formation of hydrogen bonds between ibuprofen and the thin-film surface (Zhao et al., 2017).

Figure 4-11: Contact angle of dried NF270 and TS40 membranes as a function of adsorbed ibuprofen concentration (pH 4, water flux 25 gal/ft²d, temperature 20±1°C)

Figure 4-11: Contact angle of dried NF270 and TS40 membranes as a function of adsorbed ibuprofen concentration (pH 4, water flux 25 gal/ft²d, temperature 20±1°C)
Figure 4-12 illustrates the relationship between contact angle and pH of the feed water solution for the NF270 and TS40 membranes. Error bars represent one standard deviation of uncertainty. An indirect relationship between feed water pH and contact angle was realized, ascribed by the log $K_a$ of ibuprofen. Contact angle images in Figure 4-12 provide a graphic of the decrease in membrane hydrophobicity with elevated pH. As the feed water pH was increased, less ibuprofen adsorbed onto the membrane surface as the solute transposed from the neutral to the anionic form.

Figure 4-12: Contact angle of dried NF270 and TS40 membranes as a function of feed water pH (water flux 25 gal/ft²d, temperature 20±1°C)

Figure 4-13 displays the direct relationship between the contact angle and total ibuprofen adsorbed at a 150-psi feed pressure operation. Error bars represent one standard deviation of uncertainty. Contact angle images in Figure 4-13 provide pictorial evidence of the increase in hydrophobicity.
with feed ibuprofen concentration. At the low-pressure operation, the contact angle of the membrane surface approached 69.2° with 83.7 µg/L ibuprofen adsorption. However, the high-pressure operation yielded an 82.1° contact angle measurement with 228 µg/L ibuprofen adsorption. Additional ibuprofen adsorption was indicated by an increase of contact angle, establishing a more hydrophobic membrane surface. A strong linear relationship (R² value of 0.952) suggested a direct relationship between adsorbed ibuprofen and membrane contact angle.

![Figure 4-13: Contact angle of dried NF270 membranes as a function of adsorbed ibuprofen concentration (pH 4, water flux 70 gal/ft²d, temperature 20±1°C)](image)

Figure 4-13: Contact angle of dried NF270 membranes as a function of adsorbed ibuprofen concentration (pH 4, water flux 70 gal/ft²d, temperature 20±1°C)
Adsorption Isotherm Models

Adsorption isotherms can be used to describe the relationship between the quantity of ibuprofen attached on a solid surface in relation to its surrounding aqueous concentration at a constant temperature and pressure (Howe et al., 2012). The concentration of ibuprofen adsorbed to the solid surface at equilibrium \( (q_e) \) is calculated by Equation 4-1.

\[
q_e = \frac{(C_o - C_e)V}{A}
\]

(4-1)

Where,

\( q_e \) = concentration of ibuprofen on solid surface (\( \mu g/cm^2 \))

\( C_o \) = initial concentration of ibuprofen in aqueous solution (\( \mu g/L \))

\( C_e \) = equilibrium concentration of ibuprofen in aqueous solution (\( \mu g/L \))

\( V \) = volume of aqueous solution (L)

\( A \) = surface area of solid surface (\( cm^2 \))

The Langmuir adsorption isotherm model assumes that the surface has a finite number of locations available for adsorption, attachment exchanges have the same quantity of free-energy change, and each site is capable of adsorbing one molecule of adsorbent, therefore assuming a monolayer on the surface (Langmuir, 1918). The non-linearized form of the Langmuir adsorption model is presented as Equation 4-2.

\[
q_e = \frac{q_a K_L C_e}{1 + K_L C_e}
\]

(4-2)
Where,

\[ q_a = \text{maximum adsorption capacity (\(\mu\text{g/cm}^2\))} \]

\[ K_L = \text{Langmuir adsorption constant (L/\(\mu\text{g}\))} \]

The Langmuir separation factor \((R_L)\) can determine the essential characteristics of the Langmuir isotherm, shown as Equation 4-3. Adsorption is irreversible when \(R_L\) equals 0, linear when \(R_L\) equals 1, unfavorable when \(R_L\) is greater than 1, and favorable when \(R_L\) is between 0 and 1.

\[ R_L = \frac{1}{1 + K_L C_o} \tag{4-3} \]

Where,

\[ R_L = \text{Langmuir separation factor (dimensionless)} \]

Unlike the Langmuir adsorption isotherm model, the Freundlich adsorption isotherm model assumes that each attachment exchange does not necessarily have the same quantity of free-energy change, yielding multiple layers of different adsorption energies (Freundlich, 1906). In the Freundlich model, free-energy change exponentially decreases until equilibrium is reached. The non-linearized form of the Freundlich adsorption model is presented as Equation 4-4.

\[ q_e = K_F (C_e)^{1/n} \tag{4-4} \]

Where,

\[ K_F = \text{Freundlich adsorption constant (L/cm}^2\)) \]

\[ 1/n = \text{Freundlich adsorption intensity constant, unitless} \]
Unlike the Freundlich isotherm model, the Temkin adsorption model only involves adsorbent-adsorbate interactions and assumes that the quantity of free-energy change decreases linearly with an increasing adsorption (Temkin & Pyzhev, 1940; Alsehli, 2020). The non-linearized form of the Temkin adsorption model is presented as Equation 4-5.

\[ q_e = \frac{R_u T}{b} \ln (K_T \times C_e) \]  

(4-5)

Where,

\( R_u = \) universal gas constant (8.314 J/Kmol)

\( T = \) temperature (K)

\( b = \) Temkin isotherm constant (J/mol)

\( K_T = \) Temkin isotherm equilibrium binding constant (L/µg)

Linearized forms of the adsorption isotherm models are used to determine the best-fit model for the adsorption behavior. Plotting \( 1/q_e \) as a function of \( 1/C_e \) determines the Langmuir constants \( q_a \) and \( K_L \) (shown as Equation 4-6), whereas plotting \( \log(q_e) \) as a function of \( \log(C_e) \) determines the Freundlich constants \( K_F \) and \( n \) (shown as Equation 4-7), and plotting \( q_e \) as a function of \( \ln(C_e) \) determines the Temkin constants \( b \) and \( K_T \) (shown as Equation 4-8).

\[ \frac{1}{q_e} = \frac{1}{q_a} + \frac{1}{K_L q_a C_e} \]  

(4-6)

\[ \log(q_e) = \log(K_F) + \left(\frac{1}{n}\log(C_e)\right) \]  

(4-7)

\[ q_e = \frac{R_u T}{b} \ln(K_T) + \frac{R_u T}{b} \ln(C_e) \]  

(4-8)
Feed content taken at 0 h \((C_0)\) and 24 h \((C_e)\), the volume of the solution \((10 \text{ L})\), and the surface area were used to calculate the concentration of ibuprofen on solid surface \((q_e)\). Based on the fact that ibuprofen uptake was observed when circulating the solution through the equipment without an installed coupon, the assumption that adsorption onto the membrane alone is not valid. Therefore, the surface area of the stainless-steel equipment must be included in the total surface area evaluated for adsorption. Table 4-3 presents the surface area calculations of the stainless-steel parts in the flat-sheet equipment, and the membrane coupon. Measurements include the percentage of surface that was in constant contact with feed water through each experiment.

<table>
<thead>
<tr>
<th>Title</th>
<th>Shape</th>
<th>Equation</th>
<th>Dimensions (cm)</th>
<th>Quantity</th>
<th>Area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed tank (top)</td>
<td>Cylinder</td>
<td>( A = 2\pi rh + 2\pi r^2 )</td>
<td>( r = 15.875 ) ( h = 13.335 )</td>
<td>1</td>
<td>2,914</td>
</tr>
<tr>
<td>Feed reservoir (cone)</td>
<td>Cone</td>
<td>( A = \pi r(r + \sqrt{h^2 + r^2}) )</td>
<td>( r = 15.875 ) ( h = 24.13 )</td>
<td>1</td>
<td>2,232</td>
</tr>
<tr>
<td>Chiller coil</td>
<td>Cylinder</td>
<td>( A = 2\pi rh + 2\pi r^2 )</td>
<td>( r = 0.793 ) ( h = 487.68 )</td>
<td>1</td>
<td>2,434</td>
</tr>
<tr>
<td>Tubing</td>
<td>Cylinder</td>
<td>( A = 2\pi rh + 2\pi r^2 )</td>
<td>( r = 0.793 ) ( h = 50.8 )</td>
<td>8</td>
<td>2,056</td>
</tr>
<tr>
<td>Tubing</td>
<td>Cylinder</td>
<td>( A = 2\pi rh + 2\pi r^2 )</td>
<td>( r = 0.793 ) ( h = 121.92 )</td>
<td>1</td>
<td>611</td>
</tr>
<tr>
<td>Membrane</td>
<td>Square</td>
<td>( A = l \times w )</td>
<td>( l = 9.207 ) ( w = 4.572 )</td>
<td>2</td>
<td>42</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10,331</td>
</tr>
</tbody>
</table>

Experiments were repeated to represent a total ibuprofen concentration span of 100 µg/L to 1.5 mg/L (R- and S- enantiomer range of 50 µg/L to 750 µg/L). Manipulations of \( q_e \) and \( C_e \) were plotted in accordance with the Langmuir, Freundlich, or Temkin isotherms. Adsorption isotherms were considered for equipment-ibuprofen and equipment-ibuprofen-membrane relationships.
Linearized forms of the isotherms are presented in APPENDIX F. Slopes and intercepts from the linearized forms of the isotherms were used to calculate appropriate parameters of each adsorption isotherm.

Along with the $R^2$ value, adsorption isotherm models were ascertained for error using statistical measures such as RPD (Equation 3-5), sum of the errors squared (ERRSQ, Equation 4-9) and root mean square error (RMSE, Equation 4-10).

\[
ERRSQ = \sum_{i=1}^{n} (A - T)^2
\]  
(4-9)

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{n}(A - T)^2}{n}}
\]  
(4-10)

Where,

\[n = \text{number of observations}\]

**Equipment-Ibuprofen Adsorptive Relationship**

Table 4-4 displays the adsorption isotherm parameters determined via linear analysis for the equipment-ibuprofen relationship. Parameters obtained from the linearized isotherm were used to model the concentration of R- and S- ibuprofen adsorbed onto the solid surface ($q_e$) as a function of equilibrium content in aqueous solution ($C_e$). Figure 4-14 illustrates the adsorption isotherms of R- and S- ibuprofen onto the flat-sheet equipment. For these experiments, the pink circle and blue triangle data points represent experimental adsorption data for R- and S-ibuprofen, respectively, where dashed lines denote the corresponding modeled isotherms. For each experiment, triplicate samples were taken at 24 h and averaged. Error bars represent minimum and maximum values.
from triplicate analysis. Table 4-5 displays the error analysis between experimental and modeled $q_e$ values for the Langmuir, Freundlich, and Temkin adsorption isotherms.

**Table 4-4: Adsorption isotherm parameters of equipment-ibuprofen relationship**

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>units</th>
<th>R-Ibuprofen</th>
<th>S-Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$</td>
<td>L/µg</td>
<td>$3.93 \times 10^{-3}$</td>
<td>$1.74 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$q_a$</td>
<td>µg/cm²</td>
<td>0.031</td>
<td>0.052</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>L/cm²</td>
<td>$6.35 \times 10^{-4}$</td>
<td>$5.89 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>-</td>
<td>0.566</td>
<td>0.350</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K_T$</td>
<td>L/µg</td>
<td>0.040</td>
<td>0.185</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>kJ/mol</td>
<td>$3.58 \times 10^5$</td>
<td>$2.23 \times 10^5$</td>
</tr>
</tbody>
</table>

**Figure 4-14: Adsorption isotherm curves of ibuprofen-equipment relationship**

Figure 4-14: Adsorption isotherm curves of ibuprofen-equipment relationship
Table 4-5: Error analysis for the adsorption equilibrium modeling of ibuprofen-equipment relationship

<table>
<thead>
<tr>
<th>Error function</th>
<th>R- Ibuprofen</th>
<th>S- Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
<td>Freundlich</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.993</td>
<td>0.946</td>
</tr>
<tr>
<td>RPD</td>
<td>3.73</td>
<td>9.36</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>$3.42 \times 10^{-3}$</td>
<td>$3.38 \times 10^{-3}$</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.024</td>
<td>0.024</td>
</tr>
</tbody>
</table>

The Langmuir, Freundlich, and Temkin isotherms yielded $R^2$ values greater than 0.90, authenticating adsorption equilibrium tendencies for experimental data. Favorable adsorption was observed in the Langmuir isotherm due to separation factor ($R_L$) range of 0.821 to 0.246 and 0.556 to 0.068 for R-ibuprofen and S-ibuprofen, respectively. Favorable adsorption was further verified in the Freundlich isotherm as $1/n$ values were less than 1 for R- and S-ibuprofen. Adsorption intensities denoted by adsorption constants $K_L$, $K_F$, and $K_T$ were larger for S-ibuprofen, aligning with the preferential adsorption presented herein. Furthermore, greater Langmuir maximum adsorption capacities ($q_a$) were observed for S-ibuprofen, further outlining the dissimilar enantiomer behavior.

Although the isotherms have good equilibrium adsorption predictability for ibuprofen concentration up to 350 µg/L, the models diverged in prediction of the higher equilibrium concentrations, as noted by the isotherms’ asymptotes. Error analysis revealed the Langmuir adsorption isotherm was the best fit adsorption model ($R^2$ value of 0.993 and 0.992 for R- and S-ibuprofen, respectively). Illustrated in Figure 4-14, the $q_e$ value at higher ibuprofen concentration values (greater than 350 µg/L) were well predicted via Langmuir and Temkin isotherms, but
overpredicted through the Freundlich derivation. A Langmuir adsorption model fit insinuates an equal quantity of adsorption free-energy changes and a monolayer coating of ibuprofen on the surface. Similar results have been realized in other applications utilizing stainless-steel as the adsorbent (Omanovic & Roscoe, 1999; Imamura et al., 2000; Duduna et al., 2019). Therefore, the ibuprofen-equipment relationship can be modeled via Langmuir > Temkin > Freundlich for R- and S-ibuprofen.

Equipment-Ibuprofen-Membrane Adsorptive Relationship

Table 4-6 displays the parameters determined via linear analysis for the equipment-ibuprofen-membrane relationship and Figure 4-15 illustrates the accompanying adsorption isotherms. The aforementioned sampling and analysis methodologies were applied. Table 4-7 and Table 4-8 display the error analysis for the adsorption relationships between the metal, ibuprofen, and NF270 or TS40 membrane, respectively.

Table 4-6: Adsorption isotherm parameters of equipment-ibuprofen-membrane relationship at normal operating conditions (pH 4, water flux 25 gal/ft²d, temperature 20±1°C)

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Parameter units</th>
<th>NF270</th>
<th>TS40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>R-Ibuprofen</td>
<td>S-Ibuprofen</td>
<td>R-Ibuprofen</td>
</tr>
<tr>
<td>Langmuir</td>
<td>KL</td>
<td>L/µg</td>
<td>4.08×10⁻³</td>
<td>1.44×10⁻²</td>
</tr>
<tr>
<td></td>
<td>qₐ</td>
<td>µg/cm²</td>
<td>0.033</td>
<td>0.057</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Kₚ</td>
<td>L/cm²</td>
<td>4.05×10⁻⁴</td>
<td>4.00×10⁻³</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>-</td>
<td>0.665</td>
<td>0.433</td>
</tr>
<tr>
<td>Temkin</td>
<td>Kₜ</td>
<td>L/µg</td>
<td>0.041</td>
<td>0.110</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>kJ/mol</td>
<td>3.25×10⁵</td>
<td>1.78×10⁵</td>
</tr>
</tbody>
</table>
Although Figure 4-15 and Figure 4-14 illustrate similar adsorptive behavior, it is important to note that the equipment-ibuprofen-membrane relationship displayed additional capacity to adsorb the chemical at equilibrium. Furthermore, when compared to the NF270, The TS40 membrane exhibited a larger amplitude of ibuprofen adsorption. For example, using the Temkin isotherm, at an equilibrium concentration of 800 µg/L, the adsorptive capacity of R- and S- ibuprofen onto the metal equipment was 0.024 and 0.054 µg/cm², respectively. On the contrary, at an equilibrium concentration of 800 µg/L, the adsorptive capacity of R- and S-ibuprofen onto the metal equipment with NF270 membrane was 0.026 and 0.061 µg/cm², respectively. Furthermore, the adsorptive
capacity of R- and S-ibuprofen onto the metal equipment with TS40 membrane was 0.031 and 0.079 µg/cm², respectively.

Table 4-7: Error analysis for the adsorption equilibrium modeling of equipment-ibuprofen-NF270 membrane relationship

<table>
<thead>
<tr>
<th>Error function</th>
<th>R-Ibuprofen</th>
<th>S-Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
<td>Freundlich</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.995</td>
<td>0.995</td>
</tr>
<tr>
<td>RPD</td>
<td>4.04</td>
<td>3.87</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>4.98×10^{-6}</td>
<td>4.53×10^{-6}</td>
</tr>
<tr>
<td>RMSE</td>
<td>8.43×10^{-4}</td>
<td>8.05×10^{-4}</td>
</tr>
</tbody>
</table>

Table 4-8: Error analysis for the adsorption equilibrium modeling of equipment-ibuprofen-TS40 membrane relationship

<table>
<thead>
<tr>
<th>Error function</th>
<th>R-Ibuprofen</th>
<th>S-Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir</td>
<td>Freundlich</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.996</td>
<td>0.996</td>
</tr>
<tr>
<td>RPD</td>
<td>3.76</td>
<td>2.77</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>6.67×10^{-6}</td>
<td>7.99×10^{-7}</td>
</tr>
<tr>
<td>RMSE</td>
<td>1.05×10^{-3}</td>
<td>3.65×10^{-4}</td>
</tr>
</tbody>
</table>

Langmuir, Freundlich, and Temkin isotherms for the equipment-ibuprofen-membrane relationship yielded \(R^2\) values greater than 0.900, verifying adsorption equilibrium tendencies for experimental data. Favorable adsorption of R- and S- ibuprofen was observed in both the NF270 and TS40 membrane by Langmuir \(R_L\) values between 0 and 1, and Freundlich \(1/n\) values less than 1. Additionally, larger adsorption constants were observed for S-ibuprofen, indicating greater attachment energies when compared to R-ibuprofen.
Although the three isotherms display proficiency in modeling equipment-ibuprofen-membrane adsorptive behavior at lower concentrations, the Freundlich isotherm revealed the closest representation to the range of experimental data based on error analysis. A best-fit Freundlich adsorption isotherm suggests heterogeneous free-energy changes and thus a multilayer of ibuprofen chemisorption. These findings align with existing literature denoting Freundlich-type adsorption onto a membrane surface due to its laminose structure (Liu et al., 2013a; Lin & Lee, 2014). However, it should be noted that the Langmuir and Freundlich isotherms produced analogous R² values for R-ibuprofen (0.995 for NF270, 0.996 for TS40), and similar error statistics. This suggests that as S-ibuprofen has a stronger adsorption affinity, weak interactions between R-ibuprofen and the surface may yield a thinner adsorbent layer. A study of the kinetics of R- and S-ibuprofen adsorption onto metal and membrane surfaces may elucidate the deviant adsorption mechanisms. For purposes of this work, S-ibuprofen-equipment-membrane system can be modeled via Freundlich > Temkin > Langmuir, whereas R-ibuprofen-equipment-membrane system can be modeled via Freundlich = Langmuir > Temkin.

**High-Pressure Ibuprofen Adsorption Isotherm**

In addition to the conventional low-pressure operation, the sorption of ibuprofen using the NF270 membrane under high operating pressure (150 psi) was investigated. A direct relationship between adsorption and feed concentration was realized, therefore additional attachment modeling could transpire. Table 4-9 presents the adsorption isotherm parameters determined via linear analysis for the equipment-ibuprofen-membrane relationship at high-pressure. Figure 4-16 illustrates the associated adsorption isotherms.
Table 4-9: Adsorption isotherm parameters of equipment-ibuprofen-membrane relationship at high-pressure operating conditions (pH 4, water flux 70 gal/ft\(^2\)d, temperature 20±1°C)

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>units</th>
<th>R-Ibuprofen</th>
<th>S-Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(K_L)</td>
<td>L/µg</td>
<td>5.55×10(^{-3})</td>
<td>1.95×10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>(q_a)</td>
<td>µg/cm(^2)</td>
<td>0.094</td>
<td>0.148</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(K_F)</td>
<td>L/cm(^2)</td>
<td>6.04×10(^{-3})</td>
<td>3.47×10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>(1/n)</td>
<td>-</td>
<td>0.389</td>
<td>0.217</td>
</tr>
<tr>
<td>Temkin</td>
<td>(K_T)</td>
<td>L/µg</td>
<td>0.042</td>
<td>0.451</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>kJ/mol</td>
<td>1.13×10(^5)</td>
<td>1.04×10(^5)</td>
</tr>
</tbody>
</table>

Figure 4-16: Adsorption isotherm curves of ibuprofen-equipment-NF270 membrane relationship (pH 4, water flux 70 gal/ft\(^2\)d, temperature 20±1°C)
Although low-pressure (Figure 4-15) and high-pressure (Figure 4-16) operation illustrated similar adsorptive behavior, it is important to note that the elevated operation displayed additional capacity to adsorb ibuprofen at equilibrium. For example, using the Temkin isotherm, at an equilibrium concentration of 800 µg/L, the adsorptive capacity of R- and S- ibuprofen at low feed pressure was 0.024 and 0.054 µg/cm², respectively. On the contrary, at an equilibrium concentration of 800 µg/L, the adsorptive capacity of R- and S-ibuprofen at high feed pressure was 0.080 and 0.146 µg/cm², respectively. Table 4-10 displays the error analysis conducted for the high feed pressure ibuprofen adsorption isotherms.

Table 4-10: Error analysis for the adsorption equilibrium modeling of ibuprofen onto flat-sheet equipment and NF270 membrane at high-pressure

<table>
<thead>
<tr>
<th>Error function</th>
<th>R-Ibuprofen</th>
<th>S-Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td>0.981</td>
<td>0.997</td>
</tr>
<tr>
<td>RPD</td>
<td>4.16</td>
<td>1.39</td>
</tr>
<tr>
<td>ERRSQ</td>
<td>4.65×10⁻⁵</td>
<td>3.51×10⁻⁵</td>
</tr>
<tr>
<td>RMSE</td>
<td>3.94×10⁻³</td>
<td>1.08×10⁻³</td>
</tr>
</tbody>
</table>

The ibuprofen adsorption in high-pressure operation of yielded $R^2$ values greater than 0.980, authenticating the chemical’s equilibrium attachment behavior. Favorable adsorption was also observed in the NF270 membrane by Langmuir $R_L$ values between 0 and 1, and Freundlich $1/n$ values less than 1 for R- and S- ibuprofen. Akin to the low-pressure operation, larger adsorption constants were observed for S-ibuprofen, indicating greater adsorptive energies when compared to R-ibuprofen.
The Freundlich isotherm revealed the closest representation to the range of high-pressure experimental data based on error analysis, however the Temkin isotherm also yielded comparable error analysis values, indicating predictability of both isotherms. The Langmuir isotherm underpredicted adsorptive capabilities of R- and S- ibuprofen. Therefore, the ibuprofen-equipment-membrane relationship at high-pressure can be modeled via Freundlich > Temkin > Langmuir isotherms for R- and S-ibuprofen.

*Rejection of Enantiomeric Ibuprofen in a Bench-Scale, Flat-Sheet NF Process*

The removal of R- and S- ibuprofen via NF270 and TS40 membrane was investigated extensively and results are presented herein. An initial experiment was conducted to determine the rejection of R- and S- ibuprofen at an initial total ibuprofen content of 400 µg/L (R- and S- enantiomer concentrations of 200 µg/L) in DI water adjusted to a pH of 4.0 units. Feed samples were collected at 0 and 24 h to determine the percent of rejection due to adsorption onto the flat-sheet equipment and membrane coupon. Triplicate feed concentration measurements were taken and averaged. Figure 4-17 displays the average rejection of R- and S- ibuprofen from the NF270 and TS40 membranes. Reported rejection at 24 h is presented in the blue, and impact of 24 h adsorption is illustrated in the gray. Error bars represent minimum and maximum values from triplicate analysis. The total ibuprofen rejection was 34.5 and 49.5 percent from the NF270 and TS40 membranes, respectively. As hypothesized, the larger MWCO membrane (NF270) exhibited a lower rejection than the TS40.
The adsorption of ibuprofen affects the rejection value based on the time of collection. In this work, adsorption was recorded over 24 h, and rejection was collected at 24 h. Adsorption accounted for 14.3 to 23.4 percent, and 23.6 to 31.3 percent of R-ibuprofen and S-ibuprofen rejection, respectively. It is important to note that the adsorption affected the rejection of S-ibuprofen more severely than R-ibuprofen due to the preferential affinity to the flat-sheet equipment metal components.

At a pH below 4.4 units, ibuprofen primarily exists as the neutral form, and was rejected due to adsorption and steric hindrance. It should be noted that the rejection of S-ibuprofen was greater than R-ibuprofen. Specifically, the rejection of S-ibuprofen was 10.0 and 6.77 percent higher than R-ibuprofen for the NF270 and TS40 membranes, respectively. Although CEC adsorption impacts the overall rejection, it should not impact the steric-hindrance mechanism of the membrane. This
indicates that the membrane may also have a slight affinity for the rejection of S-ibuprofen over R-ibuprofen. A possible explanation for the increased removal lies in DFT calculations, which revealed a dipole moment of 2.01 and 5.40 Debye for R- and S-ibuprofen, respectively. Existing literature suggests that a molecule’s polarity influences the orientation of the molecule relative to the membrane (Van der Bruggen et al., 1999). A molecule with a lower dipole moment is less polar, and hence contains an orientation more perpendicular to the membrane, increasing the probability of the solute to travel through the material without being rejected. Hence, the smaller dipole moment of R-ibuprofen allowed a more vertical approach, which decreased the prospect to become wedged in the membrane’s pores, lessening overall removal. Others have also found a direct relationship between CEC dipole moment and rejection (Van der Bruggen et al., 1999; Darvishmanesh et al., 2011; Shirley et al., 2014; Jeffery-Black & Duranceau, 2016b).

Effect of Feed Concentration on Enantiomeric Ibuprofen Rejection

The effect of initial ibuprofen feed concentration on ibuprofen removal was examined for a total ibuprofen content span of 75 µg/L to 2.02 mg/L (R- and S-enantiomer range of 35 µg/L to 1.01 mg/L). Experiments were conducted on the NF270 and TS40 at a 25 gal/ft²d flux (corresponding pressures of 50 and 100 psi) and the NF270 at a 70 gal/ft²d flux (pressure of 150 psi).

Figure 4-18 and Figure 4-19 present the R- and S-ibuprofen rejection as a function of feed concentration at 24 h for the NF270 and TS40 membrane, respectively. It should be noted that a logarithmic decreasing trend in rejection was exhibited as feed ibuprofen concentration increased for the TS40 membrane and NF270 experiencing high feed pressure (150 psi).
Figure 4-18: Rejection of R- and S- ibuprofen from NF270 membrane at 25 gal/ft²d (left) and 70 gal/ft²d (right) (pH 4, temperature 20±1°C)

Figure 4-19: Rejection of R- and S- ibuprofen from TS40 membrane at 25 gal/ft²d (pH 4, temperature 20±1°C)
It is known that an increase in solute feed concentration can adversely affect the solute rejection (Duranceau & Taylor, 2011; Alsalhy et al., 2013). As the feed ibuprofen concentration amplified, the content of ibuprofen adsorbed on the membrane surface increased, illustrated in Figure 4-7. At elevated feed pressures, the effect of feed concentration was more prominent. It is known that operating pressure and content of the feed water affects the concentration of solute at the membrane surface ($C_M$). Equation 2-9 specifies a direct relationship between $C_M$ and solute flux. As $C_M$ is increased, additional pressure is needed to overcome the concentration difference across the membrane, known as osmotic pressure. At a constant operating pressure, the increase of osmotic pressure causes water flux to decrease, consequently increasing permeate concentration, illustrated in Equation 2-8. In a lower pressure operation, less solute adsorbs onto the membrane, yielding a smaller $C_M$ concentration. Therefore, changes in osmotic pressure are much less discernable, leading to less or negligible decrease in rejection compared to operation at higher pressures.

**Effect of Feed Pressure on Enantiomeric Ibuprofen Rejection**

The rejection of R- and S- ibuprofen via NF270 membrane at a high-pressure condition (150 psi) was investigated extensively and results are presented herein. An initial experiment was conducted to determine the rejection of R- and S- ibuprofen at an initial total ibuprofen content of 400 µg/L (R- and S- enantiomer concentrations of 200 µg/L) in DI water adjusted to a pH of 4.0 units, pressurized at 150 psi. Figure 4-20 illustrates a comparison of average rejection of R- and S-ibuprofen from the NF270 membrane operating at 50 and 150 psi (corresponding to a water flux of 25 gal/ft²d and 70 gal/ft²d, respectively).
With an increase in feed pressure, R- and S- ibuprofen experienced a 25.7 to 36.1 and 43.4 to 64.6 rise in overall rejection, respectively. However, the enhancement in overall rejection was due to the increase of ibuprofen adsorption, mentioned in Figure 4-8. Adsorption accounted for 58.2 and 65.8 percent of the total rejection for R- and S-ibuprofen, respectively. Hence, operational pressure plays a larger role in CEC adsorption and rejection than previously understood.

Contrary to the increase in adsorption, rejection mechanized as steric hindrance decreased from 19.7 to 15.1 percent R-ibuprofen and 29.8 to 22.1 percent S-ibuprofen. Equation 2-8 illustrates a positive relationship between pressure and water flux. An elevated operating pressure increases the quantity of permeate water hence dilutes the permeate concentration, which increases rejection up to an asymptotic value. However, for organic CECs that are known to interact with the membrane surface, rejection has been perceived to decrease with increase in pressure (Nghiem et
al., 2004). As previously mentioned, feed pressure is known to affect the concentration of solute at the membrane surface ($C_M$). At lower pressures, rejection of the solute is higher because there is less driving force for the compound to permeate through the pores of the membrane surface, and hence less adsorption onto the membrane surface (Semião & Schäfer, 2011).

Although some have found that pressure does not affect solute adsorption or rejection, other research has postulated opposing findings (McCallum et al., 2008; Semião & Schäfer, 2011). Though literature on the adsorption of CECs onto NF membranes is not widely available, results obtained in bench-scale, flat-sheet experiments were compared with results of similar studies to investigate the indirect relationship between solute removal and feed pressure. Existing literature was reviewed for bench-scale, flat-sheet studies that evaluated CEC rejection from NF membranes at various feed pressures, and four studies were identified to compare the decrease of CEC rejection with an increase in driving force. Table 4-11 displays the rejection of various CECs at different pressure conditions found in existing literature. Like ibuprofen, other CECs that experienced an inverse relationship between rejection and operating pressure also exhibited adsorptive tendencies onto the membrane surface. The CECs also exude positive log $K_{ow}$ values, suggesting hydrophobic behavior in aqueous environments. However, it should be noted that adsorption is not solely based on hydrophobicity, as functional group chemistries (i.e. van der Waals forces) play an important role in adsorption. Existing literature has discovered that more polarized functional groups such as ketones can forms stronger hydrogen bonds to the membrane surface when compared to less polarized hydroxyl functional groups (Semião & Schäfer, 2011).
### Table 4-11: Hydrophobic CEC rejection at various pressures from independent literature

<table>
<thead>
<tr>
<th>CEC</th>
<th>log $K_{ow}$</th>
<th>Membrane</th>
<th>Pressure (psi)</th>
<th>Rejection (percent)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-Ibuprofen</td>
<td>3.97</td>
<td>NF270</td>
<td>50</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>S-Ibuprofen</td>
<td>3.97</td>
<td>NF270</td>
<td>50</td>
<td>29.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>22.1</td>
<td></td>
</tr>
<tr>
<td>Estrone</td>
<td>3.13</td>
<td>XN-40</td>
<td>145</td>
<td>65</td>
<td>Nghiem et al., 2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>363</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.97</td>
<td>NF200</td>
<td>72.5</td>
<td>96</td>
<td>Ducom &amp; Cabassud, 1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>435</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Estrone</td>
<td>3.13</td>
<td>NF270</td>
<td>72.5</td>
<td>85</td>
<td>Semião &amp; Schäfer, 2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>218</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>17-β-Estradiol</td>
<td>4.01</td>
<td>NF200</td>
<td>72.5</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>218</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.97</td>
<td>NF200</td>
<td>145</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>362</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>2.00</td>
<td>NF200</td>
<td>145</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>362</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Diromodichloromethane</td>
<td>2.62</td>
<td></td>
<td>145</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>362</td>
<td>93</td>
<td></td>
</tr>
</tbody>
</table>

It is important to note that independent literature examined feed operational pressures upwards of 435 psi, which is not a practical in NF application. In full-scale operation, $C_M$ accumulation prompts water purveyors to incrementally increase pressure to yield the same quantity of permeate water, which was not examined bench-scale. Therefore, full-scale systems may encounter small differences in CEC removal from incremental pressure increase.
Effect of Feed pH on Enantiomeric Ibuprofen Rejection

The effect of feed water pH on ibuprofen rejection via NF was investigated. The feed water pH was altered to 4.0, 5.0, or 6.0 units, injected with an initial racemic ibuprofen content of 1.5 mg/L (R- and S- enantiomer concentrations of 750 µg/L), and operated for 24 h. Figure 4-21 illustrates individual enantiomer rejection of ibuprofen via NF270 (left) and TS40 (right) membrane at 24 h. The rejection of S-ibuprofen is greater than its R-counterpart at the pH values examined, which can be explained by the unequal polarity of the two molecules outlined by DFT computations.

![Figure 4-21: Rejection of R- and S- ibuprofen as a function of pH for NF270 membrane (left), TS40 membrane (right) (water flux 25 gal/ft²d, temperature 20 ± 1°C)](image)

The NF270 and TS40 membranes exhibited poor rejection at feed water pH of 4.0 units. However, rejection efficacy increases with feed water pH. The feed water pH affects the speciation of ibuprofen and the magnitude of negative charge on the NF membrane (Simon et al., 2009; Ge et
al., 2017). At feed water pH values higher than 4.4 units, the membrane surface is negatively charged, and ibuprofen is dissociated, primarily existing in the anionic form. Anionic ibuprofen is rejected by the negatively charged membrane due to electrostatic repulsion and steric hinderance. Conversely, at a pH below 4.4 units, ibuprofen exists primarily as the neutral form, and the membrane surface is less negatively charged. Neutral ibuprofen is readily adsorbed onto the stainless-steel and the membrane surface. As available adsorptive sites are saturated, the membrane can partially reject neutral ibuprofen due to size exclusion. Therefore, it is reasoned that the mechanism of ibuprofen rejection at acidic conditions is initially adsorption and subsequentially steric hinderance.

Effect of Feed Water Matrix on Enantiomeric Ibuprofen Rejection

To simulate ibuprofen rejection in a natural water matrix, bulk surficial groundwater from the Town of Jupiter Utilities WTF (Jupiter, FL, USA) was collected and transported to the site of the flat-sheet equipment (UCF Water Quality Engineering Research laboratories, Orlando, FL, USA). The NGW was compared to a SGW, composed of calcium sulfate. Figure 4-22 presents a graphical comparison between the water quality of the natural and synthetic groundwater matrices (pictured left and right, respectively). It should be noted that the NGW matrix contained considerable NOM (measured by UV$_{254}$), divalent ions, and color, where the SGW matrix consisted of calcium and sulfate divalent ions.
Figure 4-22: Water quality comparison between NGW (Town of Jupiter, left) and SGW (right)

The NGW and SGW were aerated overnight to remove hydrogen sulfide and stabilize the pH to 5.0 units with 1.0 M sulfuric acid, which is representative of a WTF acidifying feed water prior to membrane treatment to prevent calcium carbonate scaling. An initial racemic ibuprofen content of 1.5 mg/L (R- and S- enantiomer concentrations of 750 µg/L) was added to the feed water and operated for 24 h. Table 4-12 presents rejection capabilities of the NF270 and TS40 flat-sheet membranes in treatment of the Town of Jupiter surficial groundwater. Although the TS40 experienced higher rejection values than the NF270, they are comparable NF treatment processes.
Table 4-12: Rejection of water quality parameters from NF270 and TS40 flat-sheet membranes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rejection (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NF270</td>
</tr>
<tr>
<td>Conductivity</td>
<td>73.3</td>
</tr>
<tr>
<td>UV₂₅₄</td>
<td>91.6</td>
</tr>
<tr>
<td>Chloride</td>
<td>4.51</td>
</tr>
<tr>
<td>Sulfate</td>
<td>95.7</td>
</tr>
<tr>
<td>Calcium</td>
<td>89.2</td>
</tr>
</tbody>
</table>

Figure 4-23 displays the rejection of R- and S- ibuprofen as a function of membrane (NF270 and TS40) and water quality matrix (control, NGW, and SGW). Operation with the NF270 and TS40 membranes are pictured left and right, respectively. The control water quality matrix represented the rejection of ibuprofen in pure DI adjusted to a pH of 5.0 units. The NF270 yielded lower R- and S- rejections than the TS40, which was formerly realized via Figure 4-17 and Figure 4-21. As previously mentioned, S-ibuprofen experienced a larger rejection due to the predominant adsorption of the enantiomer onto the flat-sheet equipment and membrane coupon. Additionally, S-ibuprofen yielded a larger rejection than R-ibuprofen due to the differences in the molecules polarity.

When compared to the control water matrix, ibuprofen rejection by the NF270 in the NGW source experienced a 16.0 and 18.1 percent increase for R- and S- ibuprofen. The TS40 displayed a comparative 20.2 and 26.4 percent increase for R- and S- ibuprofen. Others have also reported higher compound rejection in natural water matrices when compared to synthetic waters (Yoon et al., 2007; Comerton et al., 2008 Liu et al., 2013b).
Figure 4-23: Rejection of R- and S-ibuprofen from NF270 (left) and TS40 (right) membranes treating control, NGW, and SGW matrices

The increased rejection of ibuprofen in the NGW source can be elucidated by multiple interactions between NOM, the membrane surface, and ibuprofen. At feed water pH of 5.0 units, the slight negative charge on the membrane surface becomes increasingly negative as additional NOM adsorbs onto the membrane surface (Al-Amoudi et al., 2010). At said pH, 80 percent of ibuprofen persists in the anionic form. The heightened negative charge on the membrane surface enhances the electrostatic repulsion exchange with the primarily anionic ibuprofen. The cake-enhanced concentration polarization effect may also influence the rejection. As the membrane filters feed water, rejected matter (such as NOM) accrues and forms a polarization or cake-layer on the membrane surface. The cake-layer provides an additional porous layer on the membrane surface,
acting as a supplementary filter for contaminants such as ibuprofen. Additional hydrophobic interactions with the minor portion of neutral ibuprofen may also occur (Yangali-Quintanilla et al., 2009). Complexation between neutral ibuprofen and NOM may also yield larger molecules that are more difficult to remove via steric hinderance (Plakas et al., 2006).

Contrarily, when compared to the control water matrix, ibuprofen rejection in the SGW matrix with the NF270 membrane experienced a 6.83 and 12.3 percent decrease for R- and S- ibuprofen, respectively. The TS40 membrane exhibited a respective 48.7 and 41.9 percent decrease for R- and S- ibuprofen. An increase in ionic strength (due to calcium and sulfate) in a feed water matrix has been postulated to neutralize a membrane’s negative surface charge, therefore decreasing the electrostatic repulsion between the membrane and predominantly anionic ibuprofen (Comerton et al., 2009; Sadmani et al., 2014). This was not experienced in the NGW matrix due to the possible competition with NOM for sites on the membrane. Similar results have been realized for gemfibrozil (Braghetta et al., 1997). Additionally, increases in divalent ion concentration can permute the sites available for compound association, yielding decreased organic matter-compound complexation (Devitt et al., 1998).

Table 4-13 illustrates the contact angle and image of the NF270 membrane after filtering the control, NGW, and SGW matrices. Increased contact angle measurements from the NGW and SGW matrices indicate adsorption of constituents, primarily NOM and calcium from the NGW source and calcium from the SGW component. Pictured discoloration on the active area of membrane surface further verified the adsorption. Therefore, predominant NOM adsorption from the NGW matrix permitted enhanced electrostatic repulsion of ibuprofen, where the calcium from the SGW matrix affirmed decreased exclusion of ibuprofen.
Table 4-13: Contact angle and flat-sheet image of NF270 membrane treating control, NGW, and SGW matrices

<table>
<thead>
<tr>
<th>Water matrix</th>
<th>Control</th>
<th>NGW</th>
<th>SGW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (°)</td>
<td>65.8</td>
<td>98.2</td>
<td>78.5</td>
</tr>
</tbody>
</table>

**Impacts of Sample Time on Ibuprofen Rejection**

The influence of sample time is important when recording removal of neutral hydrophobic CECs like ibuprofen from a NF process. As others have agreed that 24 h is adequate for the equilibration of hydrophobic compounds. If rejection is collected within minutes of start-up, the value will not account for the adsorption of the CEC onto the membrane or equipment. Therefore, system equilibration is important in obtaining accurate removal capacities.
Existing literature on the impact of sample time when conducting removal evaluations of neutral hydrophobic CEC is scarce. Therefore, a novel mathematical model to predict ibuprofen rejection due to adsorption and steric hindrance at acidic pH conditions was developed using the regression tool in Microsoft® Excel. The model was determined using operational data reported herein. R- and S- ibuprofen concentrations were added to yield the total racemic ibuprofen concentration. Equation 4-11 presents the empirical relationship between quasi-equilibrated and initial rejection, feed concentration, adsorbed content, feed water pH, and permeate flux. Based on p-value analysis, the initial rejection, feed concentration, and amount adsorbed onto the equipment and membrane yielded most important in the relationship. Additional details regarding the cultivation of the model are presented in APPENDIX G. The model was used to recalculate ibuprofen rejection values from existing literature which did not allow their system to reach quasi-equilibrium, hence reporting overpredicted rejection capabilities of NF processes.

\[
R_{equ} = (0.014 \times C_0) - (0.069 \times (C_0 - C_e)) - (0.08 \times pH) - (0.246 \times J_w) + (0.936 \times R_{ini}) - 4.31 \quad (4-11)
\]

Where,

\[R_{equ} = \text{quasi-equilibrated ibuprofen rejection}\]

\[R_{ini} = \text{initial ibuprofen rejection}\]

Regression statistics yielded a R\(^2\) value of 0.971 at 95 percent confidence interval. Figure 4-24 illustrates a graphical representation of predicted versus experimental ibuprofen rejection values to represent the accuracy of the model.
Examining Sample Time of Rejection with Independent Sources

Results obtained in bench-scale, flat-sheet experiments were compared with published data of similar studies to investigate the importance of sample time when reporting rejection of a neutral hydrophobic CEC such as ibuprofen. Existing literature was reviewed for bench-scale, flat-sheet studies that evaluated ibuprofen rejection at pH values ± 1 pH units around its log $K_a$ (4.4) using polyamide NF membranes with congruent MWCO values to the NF270 and TS40, and four studies were identified. The selected studies contained similar stainless-steel appurtenances in their bench-scale, flat-sheet experimental setup. Furthermore, the methodologies in the research included collection of feed and permeate streams after only 1 h of operation, failing to reach an adsorption quasi-equilibrium onto the equipment and membrane surface. Therefore, the literature presented
an overestimated rejection of ibuprofen. Table 4-14 displays the operational parameters and ibuprofen rejection values of the four studies.

Table 4-14: Ibuprofen rejection from independent literature

<table>
<thead>
<tr>
<th>Ibuprofen feed concentration (µg/L)</th>
<th>Temperature (°C)</th>
<th>Permeate flux (gal/ft²d)</th>
<th>pH of feed water</th>
<th>Membrane</th>
<th>Rejection (percent)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 ± 0.1</td>
<td>31.8</td>
<td>3.5</td>
<td>NF90</td>
<td>&gt;95</td>
<td>Nghiem et al., (2006)</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>4.5</td>
<td>NF270</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.5</td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 ± 0.1</td>
<td>31.8</td>
<td>4.0</td>
<td>NF90</td>
<td>&gt;95</td>
<td>Nghiem &amp; Hawkes (2007)</td>
</tr>
<tr>
<td>750</td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>83</td>
<td>Simon et al., (2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 ± 0.1</td>
<td>31.8</td>
<td>5.0</td>
<td>NF270</td>
<td>86</td>
<td>Ge et al., (2017)</td>
</tr>
<tr>
<td>750</td>
<td></td>
<td></td>
<td></td>
<td>NF90</td>
<td>&gt;95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TFC-SR2</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF270</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.5</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.5</td>
<td>86</td>
<td></td>
</tr>
</tbody>
</table>
The removal values from the NF270 membrane in Table 4-14 were inserted into the empirical relationship to determine the extent of rejection overestimation from lack of system quasi-equilibration, illustrated in Figure 4-25. Diamonds represent ibuprofen rejection presented from independent literature. If initial and equilibrated ibuprofen rejection were equivalent, data would lie on the 45° line. However, due to removal data collection after 1 h of system equilibration, an inaccurate rejection value was reported. Ibuprofen rejection was overestimated by at 13.8 to 56.2 percent at pH of 4.0 units, at 12.4 to 41.2 percent at pH of 5.0 units, and 5.63 to 10.9 percent at pH of 6.0 units. Results from this research suggest that appropriate sample times for rejection may vary based on CEC’s physiochemical properties.

![Figure 4-25: Extent of ibuprofen overestimation from independent literature](image)
Modeling Enantiomeric Ibuprofen Rejection Utilizing HSDM

At a feed water pH of 4.0 units, ibuprofen chiefly exists in the neutral form. Neutral compounds (such as ibuprofen) can adsorb onto the membrane and subsequently diffuse through the surface to the permeate stream due to concentration potential gradients (Nghiem et al., 2005). Therefore, rejection of neutral ibuprofen can be modeled via the diffusion-based HSDM. To predict ibuprofen transport using the HSDM, water and solute MTCs were experimentally determined. The water MTC (k_w) was derived individually for each experiment due to slight variation in permeate flow rate. The ibuprofen MTC (k_s) was determined for the NF270 and TS40 membrane as the linear relationship between solute flux and the difference in ibuprofen concentration at the membrane surface and the total permeate stream, shown as Equation 2-9, and illustrated in Figure 4-26. R- and S- ibuprofen MTC derivations are pictured left and right, respectively. Feed water racemic ibuprofen content span from 75 µg/L to 1.08 mg/L (R- and S- enantiomer concentration range of 35 µg/L to 540 µg/L). Permeate values were averaged for each experiment. The HSDM-FT model was not evaluated as negligible concentrations of ions were present in the control feed water, hence most likely would not be appreciably present at the membrane surface.
Figure 4-26: NF270 and TS40 membrane R- (left) and S- (right) ibuprofen solute flux as a function of change in concentration (pH 4, temperature 20 ± 1°C)

In addition to the $k_w$ and MTC ($k_s$) values, system recovery, water flux, and the net driving pressure were derived to predict the rejection of ibuprofen through the HSDM. Table 4-15 presents the experimental parameters collected that were used to predict permeate ibuprofen concentration.

Table 4-15: Membrane operational parameters for HSDM

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NF270</th>
<th>TS40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enantiomer</td>
<td>R-Ibuprofen</td>
<td>S-Ibuprofen</td>
</tr>
<tr>
<td>$k_s$ (ft/d)</td>
<td>16.3</td>
<td>14.0</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.854</td>
<td>0.908</td>
</tr>
<tr>
<td>$J_w$ (gal/ft²/d)</td>
<td>23.7-34.4</td>
<td>20.5-27.9</td>
</tr>
<tr>
<td>R (percent)</td>
<td>0.168-0.370</td>
<td>0.234-0.329</td>
</tr>
</tbody>
</table>
The $R^2$ value for the relationships between solute flux and change in ibuprofen concentration was greater than 0.800, denoting the forced-fit regression line explained the variability for at least 80 percent of the data. Due to the larger MWCO of the NF270, R- and S- ibuprofen MTCs were an order of magnitude greater than the TS40, denoting increased mass transfer of the chemical. The S-ibuprofen MTC was also lower than that of R-ibuprofen for both membranes, indicating decreased mass transfer ascribed by preferential adsorption, yielding less total concentration to transport through the surface. Diffusional constraints (concentration) may also provide a contribution to the changes in mass transport between the two membranes. Respective parameters were inserted into the HSDM to predict permeate concentration, shown as Equation 2-11. Figure 4-27 illustrates the equilibrated versus HSDM predicted R- and S- ibuprofen permeate concentrations for the NF270 (left) and TS40 (right) membrane.

Figure 4-27: Actual vs. HSDM predicted R- and S- ibuprofen permeate concentration for NF270 (left) and TS40 (right) membranes
If the HSDM predicted ibuprofen concentration with no error, the permeate concentrations would align with the 45° line. However, it appeared that the HSDM predicted R-ibuprofen permeate concentration with some degree of accuracy, while underpredicting S-ibuprofen permeate concentration for both membranes. This was attributed by the favorable adsorption of S-ibuprofen, hence decreasing the total feed concentration of the compound over time. Reduced equilibrium feed concentration directly impacted permeate mass quantities as predicted in the HSDM as the feed parameter resides in the numerator of the HSDM function.

Actual and model predicted permeate concentrations were compared for validity using RPD and RMSE, displayed in Table 4-16. Comparatively speaking, R-ibuprofen predicted permeate values incurred much less RPD and RMSE than S-ibuprofen. However, the overall RPD was greater than 10 percent for S-ibuprofen prediction using either membrane. Therefore, the HSDM should be used with caution when predicting ibuprofen removal at acidic pH values.

In addition, a paired $t$-test with 95 percent confidence interval was performed to compare statistical difference between the actual and model predicted permeate concentrations. The null hypothesis stated that the mean of the predicted ibuprofen permeate concentration was not significantly different than the average of the actual permeate ibuprofen content. Table 4-16 presents the $t$- and $p$- values from the paired $t$-test. A $p$-value less than 0.05 is considered statistically significant and hence should be rejected. The null hypothesis was not rejected for prediction of R-ibuprofen but was rejected for S-ibuprofen. Therefore, The HSDM could predict R-ibuprofen with statistical confidence but could not be used to predict S-ibuprofen.
Table 4-16: Statistical analysis of HSDM R- and S-ibuprofen permeate concentration

<table>
<thead>
<tr>
<th>Membrane</th>
<th>NF270</th>
<th>TS40</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R-Ibuprofen</td>
<td>S-Ibuprofen</td>
</tr>
<tr>
<td>Ave. RPD</td>
<td>6.81</td>
<td>71.4</td>
</tr>
<tr>
<td>RMSE</td>
<td>20.1</td>
<td>107.5</td>
</tr>
<tr>
<td>t-value</td>
<td>0.555</td>
<td>-2.56</td>
</tr>
<tr>
<td>p-value</td>
<td>0.598</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Pilot-Scale 1,4-Dioxane Removal Experiments

In addition to the flat-sheet work, the removal of 1,4-dioxane from groundwater was evaluated using a pilot-scale, split-feed, center-port NF process housing Dupont Filmtec NF270 membranes located at the Town’s WTF (Jupiter, FL, USA). The pilot-scale unit treats natural groundwater from the Town’s surficial wellfield and encompasses dimensionally analogous hydrodynamic conditions to the full-system treatment scheme. Ibuprofen work was not conducted at the pilot-scale as it was important to monitor the adsorptive behavior in a controlled environment over a 24 h period, which was not feasible in a pilot-scale system with a required feed rate of over 260 gal/min. In addition, the pilot-scale system often endures well rotations and unexpected shutdowns, decreasing the practicality for long term experiments.

A review of 1,4-dioxane’s physiochemical properties suggest hydrophilic, non-adsorptive behavior. To verify the assumption that 1,4-dioxane would not adsorb onto the membrane surface or appurtenances, an independent experiment investigated the 24 h adsorption of 1,4-dioxane onto equipment consisting of stainless-steel and the membrane surface. Results displayed less than 5 percent adsorption of 1,4-dioxane onto the membrane surface and equipment, authenticating the
non-adsorptive behavior of 1,4-dioxane. Therefore, a NF pilot-scale investigation regarding removal of 1,4-dioxane could commence without an extensive compound equilibration period.

Although 1,4-dioxane is found naturally in some of the Town’s surficial groundwater wells at the ng/L level, a higher 1,4-dioxane concentration was needed in the feed water to effectively determine solute mass transfer and rejection. Consequently, a stock solution of 1,4-dioxane was administered into a feed basin containing existing pre-treated feed water, mixed thoroughly, and pumped into the NF pilot unit. The NF system equilibrated for 15 min prior to sample collection, based from findings of previous work (Jeffery-Black & Duranceau, 2016a). The experiments were repeated using a stock solution that provided for a total range of 1,4-dioxane concentration from 170 ng/L to 38,400 ng/L.

In addition, the rejection of 1,4-dioxane was predicted via the HSDM with and without mathematical modifications. Water MTCs were determined experimentally, and solute MTCs were determined both experimentally and empirically, then inserted into the variations of the HSDM for analysis, as illustrated previously in Figure 3-14.

Surficial Groundwater Water Quality

Feed and permeate water quality parameters were averaged over the experiments and presented in Table 4-17. Measurements were taken during each experiment to validate non-fluctuation in water quality. It is important to note that the Town’s source surficial groundwater has over 10 mg/L in dissolved organic carbon (DOC) and 120 mg/L of calcium, representing a water containing high levels of hardness and NOM, which can be effectively treated by NF.
Table 4-17: NF pilot feed and permeate water quality

<table>
<thead>
<tr>
<th>Water quality parameter</th>
<th>Feed water</th>
<th>Total permeate water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.71</td>
<td>6.59</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>26.0</td>
<td>26.4</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>850</td>
<td>540</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>590</td>
<td>370</td>
</tr>
<tr>
<td>Color (PtCo)</td>
<td>38</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>10.8</td>
<td>&lt; 0.25</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>309</td>
<td>200</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>121</td>
<td>74.2</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td>52.6</td>
<td>51.6</td>
</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>5.11</td>
<td>1.73</td>
</tr>
<tr>
<td>Sodium (mg/L)</td>
<td>22.9</td>
<td>19.6</td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>68.3</td>
<td>1.91</td>
</tr>
</tbody>
</table>

**Determination of Solute Mass Transfer Coefficient**

The 1,4-dioxane MTC was determined both experimentally and empirically. Experimental calculation of the chemical’s MTC was determined as the slope of the solute flux ($J_s$) over the change in the membrane surface 1,4-dioxane concentration to the total permeate stream, shown as Equation 2-9. Figure 4-28 illustrates the eight experimental observations plotted. Results are presented on a log-log scale due to the range of magnitude of 1,4-dioxane feed concentration. The least-squares regression method was utilized to determine the average solute MTC value of 3.92 ft/d ($1.38 \times 10^{-5}$ m/s). The $R^2$ value for the data set was 0.880, meaning the forced-fit regression line explained the variability for 88 percent of the data. The 1,4-dioxane back-transport MTC ($k_b$) was experimentally determined using Equation 2-13 and the least-squares regression method, yielding a value of 1.79 ft/d ($6.31 \times 10^{-6}$ m/s). The solute MTC of 1,4-dioxane was also calculated.
empirically using Sherwood relationships in accordance with Equation 2-23, yielding a value of 1.60 ft/d (5.64×10^{-6} m/s). However, the empirically derived solute MTC (1.60 ft/d) was slightly smaller than the experimentally derived variable (3.92 ft/d), which could be due to conservative Wilke-Chang coefficients, or non-exact dimensions of the membrane feed channel. Existing literature has realized similar results (Duranceau et al., 1992; Jeffery-Black et al., 2017).

Figure 4-28: 1,4-Dioxane solute flux as a function of change in concentration (pH 6.5, temperature 26°C; presented on log-log scale)

![Graph showing 1,4-Dioxane solute flux as a function of change in concentration](image)

\[ y = 3.92x \]
\[ R^2 = 0.884 \]

**Determination of Experimental Variables**

In addition to the solute MTC, system recovery, water flux, water MTC, and net driving pressure were required to predict the rejection of 1,4-dioxane through the HSDM or its mathematical modifications. Table 4-18 presents a summary of the experimental values obtained from the NF pilot unit experiments.
### Table 4-18: Operational variables from NF pilot for 1,4-dioxane rejection prediction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (percent)</td>
<td>85</td>
</tr>
<tr>
<td>$J_w$ (gal/ft$^2$d)</td>
<td>15.1 (25.6 L/m$^2$h)</td>
</tr>
<tr>
<td>$k_w$ (ft/d)</td>
<td>0.659 (2.32×10$^{-6}$ m/s)</td>
</tr>
<tr>
<td>$\Delta P$ (psi)</td>
<td>33.5 (2.31 bar)</td>
</tr>
<tr>
<td>$\Delta \pi$ (psi)</td>
<td>10.6 (0.730 bar)</td>
</tr>
<tr>
<td>$k_b$ (ft/d)</td>
<td>1.79 (6.31×10$^{-6}$ m/s)</td>
</tr>
<tr>
<td>$k_s$ (ft/d; experimental)</td>
<td>3.92 (1.38×10$^{-5}$ m/s)</td>
</tr>
<tr>
<td>$k_s$ (ft/d; empirical)</td>
<td>1.60 (5.64×10$^{-6}$ m/s)</td>
</tr>
</tbody>
</table>

### 1,4-Dioxane Rejection Prediction

Average actual rejection of 1,4-dioxane was 11.7 percent, which is over 24 percent lower than the findings of Kosutic et al. (2005). This difference could be due to several factors, such as the difference in membrane configuration (pilot-scale vs. flat-sheet), operational parameters (i.e. flux rate, pressure, temperature) or water matrix effects. When compared to Milli-Q water, natural water matrices have been known to decrease the rejection of CECs, specifically the presence of cations or NOM (Braghetta et al., 1997; Devitt et al., 1998; Comerton et al., 2009). However, determining rejection in a pilot-scale process fed a natural water matrix may more accurately predict actual process behavior in full-scale systems (Jeffery-Black et al., 2017).

Removal of 1,4-dioxane was predicted through the HSDM and modifications (Equation 2-11 to 2-17). Average rejection percentages from each model are illustrated in Figure 4-29. Error bars represent one standard deviation of uncertainty. The average actual rejection of 1,4-dioxane from the eight experiments was 11.7 percent, whereas the average HSDM predicted rejection of 1,4-
dioxane was 12.5 percent. From Figure 4-29, the HSDM-FT, IOPM, SH-HSDM-FT, and SH-IOPM under-predicted 1,4-dioxane rejection, while IHSDM, IOPM-FT, SH-HSDM, SH-IHSDM, and SH-IOPM-FT over-predicted 1,4-dioxane rejection. The IHSDM-FT and SH-IHSDM-FT severely under-predicted 1,4-dioxane permeate concentration and are thus not shown in the figure.

Figure 4-29: Average rejections for diffusion-based models

**1,4-Dioxane Permeate Concentration Prediction**

It should be noted that the method used to derive the solute MTC influences the prediction of 1,4-dioxane permeate concentration. As earlier mentioned, the solute MTC can be derived experimentally or empirically. Figure 4-30 shows the actual versus HSDM-predicted 1,4-dioxane permeate concentration with the 1,4-dioxane MTC calculated experimentally (HSDM) and empirically (SH-HSDM). Results are plotted on a log-log scale due to the range in 1,4-dioxane
concentration. If the models predicted 1,4-dioxane permeate concentration with no error, the permeate concentrations would align with the 45° line. Permeate concentration of 1,4-dioxane was predicted within ±8 percent using the HSDM but was consistently under-predicted using the SH-HSDM. As mentioned earlier, conservative Wilke-Chang coefficients or non-exact membrane dimensions may have contributed to the inaccuracy in 1,4-dioxane permeate prediction for the SH-HSDM. Although the empirically derived MTC yielded an underprediction in 1,4-dioxane permeate concentration, derivation of the value required no prior operational data, which can be attractive when predicting permeate concentration without an existing operational bench-scale or pilot-scale system.

Figure 4-30: Actual vs. predicted 1,4-dioxane permeate concentration using HSDM and SH-HSDM (presented on log-log scale)
Actual and model predicted permeate concentrations were compared for validity using relative percent difference (RPD) and root mean square error (RMSE). Figure 4-31 presents the RPD range and RMSE value for the diffusion-based predictability of 1,4-dioxane permeate content, compared to the actual permeate concentration determined from the pilot-scale experiments. The HSDM, HSDM-FT, IOPM, and SH-HSDM-FT resulted in RPD values less than ±10 percent and RMSE less than 2.0. Whereas, the IHSDM, IOPM-FT, SH-HSDM, SH-IHSDM, and SH-IOPM-FT incurred larger RPD and RMSE values, suggesting such modifications of the HSDM should not be considered to model the rejection of 1,4-dioxane in a NF process.

Figure 4-31: RPD range and RMSE for HSDM models
In addition, a paired $t$-test with 95 percent confidence interval was performed to compare statistical difference between the actual and model predicted permeate concentrations. The null hypothesis stated that the mean of the predicted permeate concentration was not significantly different than the average of the actual permeate content. Table 4-19 displays the results from the paired $t$-test at a 95 percent confidence interval. The null hypothesis was not rejected for the HSDM, HSDM-FT, IOPM, and SH-HSDM-FT. Hence, the IHSDM, IHSDM-FT, IOPM-FT, SH-HSDM, SH-HSDM-FT, and SH-IOPM-FT should not be considered to accurately predict 1,4-dioxane rejection in a NF process.

<table>
<thead>
<tr>
<th>Model</th>
<th>$t$-value</th>
<th>$p$-value</th>
<th>Statistically significant difference? (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental $k_s$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSDM</td>
<td>-0.82</td>
<td>0.437</td>
<td>N</td>
</tr>
<tr>
<td>HSDM-FT</td>
<td>2.14</td>
<td>0.070</td>
<td>N</td>
</tr>
<tr>
<td>IHSDM</td>
<td>-2.93</td>
<td>0.022</td>
<td>Y</td>
</tr>
<tr>
<td>IHSDM-FT</td>
<td>-2.77</td>
<td>0.027</td>
<td>Y</td>
</tr>
<tr>
<td>IOPM</td>
<td>0.805</td>
<td>0.447</td>
<td>N</td>
</tr>
<tr>
<td>IOPM-FT</td>
<td>-2.92</td>
<td>0.023</td>
<td>Y</td>
</tr>
<tr>
<td>Empirical $k_s$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSDM</td>
<td>-2.91</td>
<td>0.022</td>
<td>Y</td>
</tr>
<tr>
<td>HSDM-FT</td>
<td>1.08</td>
<td>0.314</td>
<td>N</td>
</tr>
<tr>
<td>IHSDM</td>
<td>-2.84</td>
<td>0.025</td>
<td>Y</td>
</tr>
<tr>
<td>IHSDM-FT</td>
<td>-2.77</td>
<td>0.027</td>
<td>Y</td>
</tr>
<tr>
<td>IOPM</td>
<td>2.35</td>
<td>0.051</td>
<td>N</td>
</tr>
<tr>
<td>IOPM-FT</td>
<td>-2.92</td>
<td>0.022</td>
<td>Y</td>
</tr>
</tbody>
</table>

Based on the average predicted rejection, RPD, RMSE, and paired $t$-test, the models best fit to predict 1,4-dioxane rejection in a NF process are: HSDM > IOPM > SH-HSDM-FT > HSDM-FT > SH-IOPM. The results indicate the FT parameter in the model did not significantly improve
rejection prediction, suggesting negligible effects of concentration polarization on the mass transfer of 1,4-dioxane through a NF membrane. This could possibly be due to high water flux rate, low operational pressure, and low TDS concentration of the NF feed water, or neutral charge of 1,4-dioxane, also realized by others (Zhao & Taylor, 2005; Jeffery-Black et al., 2017). The addition of an instantaneous feed parameter into the HSDM (IHSDM) decreased the accuracy of 1,4-dioxane rejection. The addition of an instantaneous flux, pressure, and osmotic pressure term (IOPM) yielded similar results to the HSDM, proposing that the addition of such variables incurred little effect in increasing the accuracy of 1,4-dioxane rejection prediction.
CHAPTER 5. SUMMARY AND CONCLUSIONS

Summary

This research reported upon in this dissertation presents the methods used and results obtained of an investigation into the rejection and mass transfer of ibuprofen enantiomers and 1,4-dioxane using a NF membrane process. Bench-scale (flat-sheet) and pilot-scale (spiral-wound) testing configurations were relied on to collect information during the study of the removal of the two CECs in aqueous solution by membrane processes. Mathematical models were developed to explain mass transfer and serve as predictive tools for determining solute removal capabilities of membrane treatment.

The results of this study revealed the atypical behavior of R- and S- ibuprofen enantiomers in aqueous solutions being treated by NF processes. Although the enantiomers of ibuprofen contain equivalent chemical properties and were delivered as a racemic mixture, S-ibuprofen adsorbed up to 5 times more than R-ibuprofen onto stainless-steel and showed preferential rejection in a NF process. DFT calculations unveiled supporting evidence to the differing behavior of the enantiomers in terms of molecular volume and dipole moment. Ibuprofen adsorption was found to increase with feed concentration and pressure and decrease with elevated feed pH. Ibuprofen adsorption was also observed on the membrane, verified by an increase in surface hydrophobicity compared to that of the compacted material with DI. Adsorption isotherms were employed to model the ibuprofen-adsorbent relationships. The ibuprofen-equipment relationship with and without the membrane coupon were best described by the Freundlich and Langmuir isotherms, respectively. The total ibuprofen rejection at a feed water pH of 4.0 units was 34.5 and 49.5 percent.
from the NF270 and TS40 membrane, respectively, and believed to be due to adsorption and steric hindrance. Adsorption onto the surfaces influenced NF270 and TS40 rejection by 27.3 and 18.9 percent, respectively. Ibuprofen rejection was found to increase with feed water pH, elevated feed pressure, and NOM concentration, and decrease with calcium content. Diffusion-based HSDM modeling was attempted for R- and S- ibuprofen, yielding moderate success for the R- enantiomer, but was unsuccessful for the S-counterpart due to the extent of adsorption that could not be accounted for in the HSDM.

Results from this research validated membrane studies performed with less than 24 h of equilibration time can result in overpredicted contaminant removal values. This finding agrees with the work of Kimura and colleagues (2003b) that demonstrated 24 h of operation was adequate for equilibration of hydrophobic compounds. This work also revealed that longer equilibration times may be required to reach complete saturation in the case of the CEC ibuprofen. Appropriate sample times for rejection may vary based on CEC’s physiochemical properties.

Additionally, rejection of 1,4-dioxane through a 0.385 MGD split-feed, center-port NF pilot unit treating surficial groundwater was determined to be approximately 11.7 percent. Rejection did not vary by solute concentration when water flux and temperature were held constant. Diffusion-based mass transfer models such as the HSDM, HSDM-FT, IHSDM, IHSDM-FT, IOPM, and IOPM-FT were used to predict 1,4-dioxane permeate. Model predicted permeate concentration was ascertained for validity by comparing to actual permeate concentration by statistical error analysis, revealing the HSDM model to be the most proficient in modeling 1,4-dioxane permeate concentration.
Conclusions

1. Although ibuprofen was previously known to adsorb onto membrane surfaces at feed water pH values below its log $K_a$, ibuprofen was also found to attach onto the bench-scale, flat-sheet equipment, that included stainless-steel materials of construction. In a control experiment, 23 percent of ibuprofen was lost after 24 h of operation. It was hypothesized that ibuprofen adsorbed onto the stainless-steel of the flat-sheet equipment. Prior research appears to support this finding as other studies have highlighted ibuprofen’s capacity to adsorb onto metal surfaces, such as copper and chromium-based metal-organic frameworks.

2. S-ibuprofen displayed a stronger affinity to adsorb onto the flat-sheet equipment when compared to its counterpart, R-ibuprofen. At an initial racemic ibuprofen concentration of 100 µg/L, S-ibuprofen adsorbed 4.82 times more than R-ibuprofen. The ratio fell to 2.25 at an initial racemic ibuprofen concentration of 1,550 µg/L. A possible explanation for the disparate behavior of enantiomers resided in DFT computations, which yielded a 6.40 Å$^3$ smaller molecular volume and 3.39 longer Debye dipole moment of S-ibuprofen than R-ibuprofen, alluding to the less hindered travel and stronger affinity to adsorb onto the stainless-steel of the flat-sheet equipment.

3. The adsorption of R- and S- ibuprofen were influenced by membrane type, initial feed concentration, operating pressure, and feed pH. Enantiomers of ibuprofen were found to adsorb to the flat-sheet equipment’s materials of construction as well as the actual membrane coupon when inserted into the bench-scale setup. The initial feed ibuprofen concentration yielded a positive direct relationship with the concentration of ibuprofen
adsorbed. Of the two membranes tested, the tighter TS40 contained a larger adsorptive capacity compared to the NF270, which may be explained by the thickness of the active layer or the affinity of the material to form hydrogen bonds with ibuprofen. Contact angle measurements revealed a direct relationship between membrane hydrophobicity and adsorbed ibuprofen concentration. Similar findings were discovered for operation at an increased feed pressure. An increase in the pH of the feed water yielded a decrease in adsorbed ibuprofen, as it was assumed that neutral ibuprofen was primarily responsible for the adsorption, while anionic ibuprofen repelled both the membrane and metal surface.

4. *Isotherms successfully modeled the adsorption of R- and S- ibuprofen to the flat-sheet equipment and membrane coupon.* Langmuir, Freundlich, and Temkin isotherms were elected to model the adsorptive behavior of R- and S- ibuprofen onto the flat-sheet equipment with and without a membrane coupon installed. While the selected isotherms yielded $R^2$ values greater than 0.900, additional error analysis revealed that the Langmuir and Freundlich isotherms were the best fit to model the equipment-ibuprofen and equipment-ibuprofen-membrane relationships, respectively.

5. *The rejection of S-ibuprofen was greater than R-ibuprofen.* For example, at a feed water pH of 4.0 units and injected racemic ibuprofen concentration of 400 µg/L, the rejection of S-ibuprofen was 10.0 and 6.77 percent higher than R-ibuprofen for the NF270 and TS40 membranes, respectively. The disparity could be explained by the DFT computations, which disseminated a dipole moment of 2.01 and 5.40 Debye for R- and S- ibuprofen, respectively. As literature has postulated that polarity influences the orientation of the molecule relative to the membrane surface, the smaller dipole moment of R-ibuprofen
yielded a more perpendicular approach, which increased the probability of the molecule to travel through the material without being rejected.

6. The rejection of R- and S-ibuprofen were influenced by membrane type, initial feed concentration, operational pressure, feed pH, and feed water matrix. Compared to the NF270, the rejection of ibuprofen at a pH of 4.0 units was 15 percent higher using the TS40, due to the tighter MWCO. As the feed concentration increased, the rejection decreased for the TS40 and high-pressure NF270 experiments. Increased feed pressure increased the concentration of ibuprofen onto the membrane surface (C_M), subsequently elevating osmotic pressure, therefore decreasing solute flux and rejection. Conversely, an increase in feed water pH yielded a positive relationship with ibuprofen rejection. As the pH of feed water was increased above ibuprofen’s log K_a, it became more anionic, allowing the negatively charged membrane surface to reject the CEC via electrostatic repulsion. The persistence of NOM in feed water matrix increased ibuprofen rejection as the adsorbed matter enhanced electrostatic interaction between ibuprofen and the membrane surface. Contrarily, the presence of calcium in the feed water matrix decreased ibuprofen rejection by neutralizing the charge on the membrane, thus depressing the electrostatic repulsion between the chemical and the surface.

7. Sampling time plays an important role in determining the removal mechanism of hydrophobic CECs from a membrane process. After 24 h of operation, adsorption accounted for 14.3 to 23.4 percent of R-ibuprofen and 23.6 to 31.3 percent of S-ibuprofen removal. Rejection of hydrophobic CECs like ibuprofen was believed to have decreased over time due to the saturation of adsorption sites on the metal and membrane surface.
Therefore, the time that samples are collected may provide insight to the removal mechanism of ibuprofen. A novel mathematical model for predicting ibuprofen rejection after quasi-equilibration, with an adjusted $R^2$ of 0.981 at a 95 percent confidence interval, was developed utilizing experimental data including initial concentration and rejection, adsorbed content, feed water pH, and permeate flux. Ibuprofen rejection values after 1 h of equilibration time from existing literature were inserted into the model to determine the extent of overcalculation from collecting removal data prior to sufficient adsorption. Results yielded ibuprofen rejection overestimation of 5.63 to 56.2 percent, which highlights the importance of understanding the kinetic behavior of hydrophobic CECs like ibuprofen when evaluating the removal effectiveness of a water treatment process.

8. *Rejection of R- and S- ibuprofen was modeled with limited success using the HSDM.* As the solute transport mechanism for ibuprofen was believed to be due to concentration potential gradients (and hence diffusion), the removal of the chemical could be modeled by the HSDM. The S-ibuprofen MTC value was reported less than that of R-ibuprofen, indicating decreased mass transfer of the S-enantiomer ascribed by preferential adsorption, yielding less total concentration for transport. Diffusional constraints may have also provided a contribution to the changes in mass transport. Results indicated that the HSDM predicted R-ibuprofen permeate concentration with some degree of accuracy, while the diffusion-based model severely underpredicted S-ibuprofen permeate concentration for both NF270 and TS40 membranes.

9. *Rejection of 1,4-dioxane in a pilot-scale NF membrane process treating surficial groundwater was 11.7 percent. Rejection did not vary with increasing concentration.*
Rejection was successfully modeled using the HSDM. As 1,4-dioxane is a small neutral hydrophilic chemical, it was hypothesized that the rejection from a loose NF membrane would be low (less than 30 percent). Frequent source water detection compounded with looming governmental regulation may prompt water purveyors to elect additional treatment processes to reject or degrade the CEC, such as RO, advanced oxidation, or adsorption. As it was hypothesized that 1,4-dioxane diffused through the membrane, the rejection could be modeled via the HSDM. Experimental and empirical calculations of the solute MTC were derived, and the empirically derived value was found to be 2.32 ft/d less than the experimental figure, possibly due to conservative Wilke-Chang coefficients, or non-exact dimensions of the membrane feed channel. Predictive modeling with the HSDM and mathematical modifications proved somewhat successful, with the HSDM, IOPM, and SH-HSDM-FT incurring the least statistical error. Results suggested that the addition of the FT value, or instantaneous feed, flux, and pressure parameters had little effect in increasing the accuracy of 1,4-dioxane rejection.
CHAPTER 6. RECOMMENDATIONS

The results generated in this work elicit important points that should be considered when conducting future research regarding CECs and their interactions and behavior in membrane processes.

- When conducting compound rejection studies using bench-scale, flat-sheet equipment, it is important to understand the chemical properties of the compound, and conduct mass balance experiments to determine if solute concentration loss will occur. Possible loss of compound due to volatilization or adsorption should be noted and accounted to prevent inaccurate documentation of rejection efficacy. As adsorption of neutral hydrophobic CECs greatly influences rejection, a mass balance test is recommended to be performed with these types of chemicals dissolved in natural waters.

- It is important to allow full-scale membrane treatment systems to fully equilibrate prior to conducting hydrophobic CEC solute rejection studies. Rejection of hydrophobic CECs like ibuprofen may decrease over time due to the saturation of adsorption sites on metal and membrane surfaces. It is recommended that rejection evaluations be conducted after system start-up, as this specific research phase may be more indicative of the steric hindrance capabilities of the process (as opposed to adsorptive capacities). Although equilibration times are typically not known in full-scale systems, a rough estimate can be obtained from Equation 6-1.

\[ \frac{1}{day} = \frac{q_a \times A}{C_F \times Q} \]  

6-1

Where,
Maximum solute adsorptive capacity ($q_a$) of hydrophobic CECs onto membrane surfaces should be experimentally determined. Additionally, the relationship between maximum adsorption capacity of a membrane and thickness of the active layer of the membrane or
the affinity of the material of the membrane to form hydrogen bonds with hydrophobic CECs could be investigated to provide further understanding into this phenomenon.

- The feasibility of ibuprofen, along with other neutral hydrophobic CECs, should be examined for application regarding corrosion control. In the water treatment realm, corrosion control is integral to the structural integrity of distribution systems that convey potable water to consumers. Rather than releasing ibuprofen and other hydrophobic CECs into the environment, recovering and utilizing the compound to sustain robustness of water distribution systems is a novel inkling to be investigated.
APPENDIX A. DESALINATION AND WATER TREATMENT
COPYRIGHT PERMISSION LETTER
July 9, 2020

To whom it may concern:

I hereby grant permission to reproduce material from the following publication

"Modeling the mass transfer of 1,4-dioxane in a nanofiltration membrane process" by Carlyn J. Higgins and Steven J. Duranceau


for inclusion in the dissertation of Carlyn J. Higgins.

I request that relevant reference to Desalination and Water Treatment be made.

With best wishes,

[Signature]

Miriam Balaban, editor-in-chief
Desalination and Water Treatment
www.deswater.com
Recovery and Rejection

Recovery (R) describes the percentage of feed water that is treated to permeate. Rejection (r) describes the percentage of solute that was removed from the feed stream by the membrane. An example of recovery and rejection are calculated from Equations 2-3 and 2-4, respectively using values from a single pilot-scale 1,4-dioxane experiment.

\[
R = \left( \frac{Q_P}{Q_F} \right) \times 100
\]  
(2-3)

\[
r = \frac{C_F - C_P}{C_F} \times 100
\]  
(2-4)

\[
R = \frac{226 \text{ gal min}^{-1}}{267 \text{ gal min}^{-1}} \times 100 = 84.6 \text{ percent}
\]

\[
r = \frac{180 \text{ ng L}^{-1} - 150 \text{ ng L}^{-1}}{180 \text{ ng L}^{-1}} \times 100 = 16.7 \text{ percent}
\]

Water Flux and Water Mass Transfer Coefficient

Water flux (\(J_w\)) defines the rate in which permeate flows through a membrane. The water MTC (\(k_w\)) is a diffusion rate constant that relates water permeation rate and driving force (pressure). An example of water flux and the associated MTC is calculated from Equation 2-8, using data from a single pilot-scale 1,4-dioxane experiment.

\[
J_w = k_w(\Delta P - \Delta \pi) = \frac{Q_P}{A}
\]  
(2-8)

\[
J_w = \left( \frac{226 \text{ gal min}^{-1}}{21,600 \text{ ft}^2 \text{ day}^{-1}} \right) \times \left( 1440 \text{ min day}^{-1} \right) = 15.1 \text{ gal ft}^{-2} \text{ d}^{-1}
\]
\[
k_w = \frac{J_w}{(\Delta P - \Delta \pi)} = \frac{15.1 \text{ gal}}{ft^2d} \left(\frac{33.5 \text{ psi} - 10.6 \text{ psi}}{22.9 \text{ psi}}\right) \times \left(\frac{ft^2}{144\text{in}^2}\right) \times \left(\frac{8.35 \text{ lb}}{gal}\right) = 0.038/\text{day}
\]

Solute Flux and Solute Mass Transfer Coefficient

Solute flux \((J_s)\) describes the rate in which a contaminant permeates through a membrane. The solute MTC \((k_s)\) is a diffusion rate constant that relates the solute permeation rate and associated concentration difference between the membrane surface and permeate stream. An example of solute flux and accompanying MTC is calculated by Equation 2-9, using data from a single pilot-scale 1,4-dioxane experiment.

\[
J_s = k_s(C_{FC} - C_p) = k_s \left[ \frac{C_F + C_C}{2} - C_p \right] = \frac{Q_p C_p}{A}
\]

\[
J_s = \left(\frac{226 \text{ gal}}{\text{min}}\right) \times \left(\frac{150 \text{ ng}}{L}\right) \times \left(\frac{1440 \text{ min}}{\text{day}}\right) \times \left(\frac{3.785 L}{1 \text{ gal}}\right) \times \left(\frac{lb}{4.54 \times 10^{11} \text{ng}}\right) = 1.9 \times 10^{-8} \frac{lb}{ft^2d}
\]

\[
k_s = \frac{J_s}{(C_{FC} - C_p)} = \frac{1.9 \times 10^{-8} \frac{lb}{ft^2d}}{\left(\frac{180 \text{ng}}{L} + 320 \text{ng}}{L}\right) - 150 \frac{\text{ng}}{L}} \times \frac{1}{6.243 \times 10^{-11} \frac{lb}{ft^3}} = 3.04 \frac{ft}{d}
\]

Crossflow Velocity

Crossflow velocity is the linear rate of the feed flow tangent to the membrane surface. An example of crossflow velocity is calculated in the CF042 cell housing the NF membrane coupons in the flat-sheet setup.
\[ v = \frac{Q}{A} = \frac{1}{0.23cm \times 3.92cm} \left( \frac{1min}{60 sec} \right) \left( \frac{1cm^2}{1.08 \times 10^{-3} ft^2} \right) \left( \frac{0.0353 ft^3}{1L} \right) = 0.590 \frac{ft}{s} \]

Sherwood Number

The solute MTC can be determined experimentally using Equation 2-9 or, empirically using Sherwood relationships. An example of the solute MTC is calculated by Equations 2-18 to 2-23 using data from a single pilot-scale 1,4-dioxane experiment.

The hydraulic diameter \( d_h \) was calculated using Equation 2-22, based on an 8" Dupont Filmtec NF270 membrane. The membrane length, membrane width, and feed channel spacer height were provided by Dupont Water Solutions (Edina, MN, USA).

\[ d_h = 4 \left( \frac{xy}{2(x+y)} \right) \]

\[ d_h = 4 \left( \frac{(120ft) \times (0.0023ft)}{2(120ft + 0.0023ft)} \right) = 0.0047ft \]

Area \( A \) was calculated by multiplying the feed channel spacer height by the membrane channel width. Feed velocity \( v \) was calculated by the average feed flow through the first stage pressure vessels, yielding a value of 14.2 gal/min (0.032 ft³/s).

\[ A = x \times y \]

\[ A = 0.0023ft \times 120ft = 0.276 ft^2 \]

\[ v = \frac{Q}{A} \]
\[ v = \frac{0.032 ft^3}{0.276 ft^2 s} = 0.116 \frac{ft}{s} \]

The Reynolds number \( (R_e) \), shown as Equation 2-19 was calculated using hydraulic diameter, feed channel velocity, density of water, and viscosity of feed water. At a feed water temperature of 25°C (298 K), the viscosity of water is \( 8.937 \times 10^{-4} \) kg/ms.

\[
R_e = \frac{d_h v p}{\mu} \tag{2-19}
\]

\[
R_e = \frac{0.0047 ft \times 0.116 \frac{ft}{s} \times 997 \frac{kg}{m^3} \left( \frac{1 m^2}{10.78 ft^2} \right)}{8.937 \times 10^{-4} \frac{kg}{m - s}} = 56.4
\]

The diffusivity \( (D_i) \) of 1,4-dioxane can be calculated using Wilke-Chang relationships, listed as Equation 2-21 (Wilke & Chang, 1955). The 1,4-dioxane molal volume \( (V_i) \) can be calculated using atomic volumes for 1,4-dioxane, with a molecular formula of \( C_4H_8O_2 \).

\[
V_i = (4) \times \left( 0.0148 \frac{m^3}{kmol} \right) + (8) \times \left( 0.0037 \frac{m^3}{kmol} \right) + (2) \times \left( 0.001429 \frac{m^3}{kmol} \right) = 0.09166 \frac{m^3}{kmol}
\]

\[
D_i = \frac{(117.3 \times 10^{-18})[(\varphi)(MW)]^{0.5}(T)}{\mu V_i^{0.6}} \tag{2-21}
\]

\[
D_i = \frac{(117.3 \times 10^{-18})[(2.26)\left( 18 \frac{kg}{k mol} \right)]^{0.5}(298 K)}{8.937 \times 10^{-4} \frac{kg}{m - s} \times (0.09166 \frac{m^3}{kmol})^{0.6}} = 1.08 \times 10^{-9} \frac{m^2}{s}
\]

The Schmidt number \( (S_c) \), shown as Equation 2-20 can be calculated using feed water viscosity, water density, and 1,4-dioxane diffusivity.

\[
S_c = \frac{\mu}{\rho D_i} \tag{2-20}
\]
The Sherwood number \( (S_h) \) listed as Equation 2-18 is calculated via a direct relationship between the Reynolds number, Schmidt number, hydraulic diameter, and length of membrane (Sherwood et al., 1967).

\[
S_h = 1.86 \left( \frac{ReSc}{L_m} \right)^{0.33}
\]

\[
S_h = 1.86 \left( \frac{56.4 \times 830 \times 0.0047}{3.16 f_t} \right)^{0.33} = 7.54
\]

The solute MTC \( (k_s) \) can then be empirically calculated using Sherwood number, 1,4-dioxane diffusivity, and hydraulic diameter, shown as Equation 2-23.

\[
k_s = \frac{S_h D_t}{d_h}
\]

\[
k_s = \frac{7.54 \times 1.08 \times 10^{-9} m^2}{0.0047 f_t} \times \left( \frac{86,400 s}{1 d} \right) \left( \frac{10.78 ft^2}{m^2} \right) = 1.60 \frac{ft}{d}
\]

**HSDM**

In a diffusion-based membrane process, permeate concentration can be predicted using the HSDM, shown as Equation 2-11. An example calculation is presented using the HSDM on a single 1,4-dioxane pilot-scale experiment.

\[
C_p = \frac{k_s C_F}{k_w (\Delta P - \Delta \pi) \left( \frac{1}{2} - \frac{2R}{2 - R} \right) + k_s}
\]
In a diffusion-based membrane process treating water with the capacity to form an accumulation of rejected solute near the membrane surface, permeate concentration can be predicted using the HSDM-FT, shown as Equation 2-12. An example calculation is presented using the HSDM-FT on a single 1,4-dioxane pilot-scale experiment.

\[ C_P = \frac{k_s C_F \exp \left( \frac{J_w}{k_b} \right)}{k_w(\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s \exp \left( \frac{J_w}{k_b} \right)} \]

\[ C_P = \frac{\left(3.92 \frac{ft}{d}\right) \left(1.1 \times 10^{-8} \frac{lb}{ft^3}\right)}{0.0898 \frac{ft}{d} \text{psi} \left(33.5 \text{psi} - 10.6 \text{psi}\right) \left( \frac{2 - (2 \times 0.846)}{2 - 0.846} \right) + 3.92 \frac{ft}{d}} = 9.649 \times 10^{-9} \frac{lb}{ft^3} = 155 \frac{ng}{L} \]

**HSDM-FT**

In a diffusion-based membrane process treating water with the capacity to form an accumulation of rejected solute near the membrane surface, permeate concentration can be predicted using the HSDM-FT, shown as Equation 2-12. An example calculation is presented using the HSDM-FT on a single 1,4-dioxane pilot-scale experiment.

\[ C_P = \frac{k_s C_F \exp \left( \frac{J_w}{k_b} \right)}{k_w(\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s \exp \left( \frac{J_w}{k_b} \right)} \]

\[ C_P = \frac{\left(3.92 \frac{ft}{d}\right) \left(1.1 \times 10^{-8} \frac{lb}{ft^3}\right)}{0.0898 \frac{ft}{d} \text{psi} \left(33.5 \text{psi} - 10.6 \text{psi}\right) \left( \frac{2 - (2 \times 0.846)}{2 - 0.846} \right) + 3.92 \frac{ft}{d} \exp \left( \frac{2.01 \frac{ft}{d}}{1.79 \frac{ft}{d}} \right)} = 1.05 \times 10^{-8} \frac{lb}{ft^3} = 169 \frac{ng}{L} \]

**IOPM**

In a diffusion-based membrane process, permeate concentration can be predicted using the IOPM, shown as Equation 2-16. An example calculation is presented using the IOPM on a single 1,4-dioxane pilot-scale experiment.

\[ C_P = \frac{C_F}{R} \left\{ 1 - \left[ \frac{\Delta P - k_{TDS} \cdot TDS_C}{\Delta P - k_{TDS} \cdot TDS_F (1 - R)} \right]^{\frac{k_s}{k_w \Delta P + k_s}} \right\} \]

\[ C_P = \frac{C_F}{R} \left\{ 1 - \left[ \frac{\Delta P - k_{TDS} \cdot TDS_C}{\Delta P - k_{TDS} \cdot TDS_F (1 - R)} \right]^{\frac{k_s}{k_w \Delta P + k_s}} \right\} \]

(2-16)
\[ C_P = \frac{1.1 \times 10^{-8}}{0.846} \frac{\text{lb}}{\text{ft}^3} \left \{ 1 - \frac{33.5 \text{psi} - 13.58 \text{psi}}{33.5 \text{psi} - 5.64 \text{psi}} (1 - 0.846) \right \} \]

\[ \frac{3.92 \frac{\text{ft}}{\text{psi}}}{0.0896 \frac{\text{ft}}{\text{psi}^2} 33.5 \text{psi} + 3.92 \frac{\text{ft}}{\text{psi}}} \right \} \]

\[ 9.86 \times 10^{-9} \frac{\text{lb}}{\text{ft}^3} = 158 \text{ ng L}^{-1} \]

IOPM-FT

In a diffusion-based membrane process treating water with the capacity to form an accumulation of rejected solute near the membrane surface, permeate concentration can be predicted using the IOPM-FT, shown as Equation 2-17. An example calculation is presented using the HSDM-FT on a single 1,4-dioxane pilot-scale experiment.

\[ C_P = \frac{C_F}{R} \left \{ 1 - \frac{\Delta P - k_{TDS} * TDS_C}{\Delta P - k_{TDS} * TDS_F} \frac{k_s}{k_{w} \Delta P} (1 - R) \right \} \]

\[ \left \{ 1 - \frac{\exp\left[\frac{L_J}{k_{w} \Delta P}\right]}{\exp\left[\frac{L_J}{k_{b} \Delta P}\right]} \right \} \]

\[ 8.36 \times 10^{-9} \frac{\text{lb}}{\text{ft}^3} = 134 \text{ ng L}^{-1} \]

IHSDM

In a diffusion-based membrane process, permeate concentration can be predicted using the IHSDM, shown as Equation 2-14. An example calculation is presented using the IOPM on a single 1,4-dioxane pilot-scale experiment.

\[ C_P = \frac{k_s C_F}{-R J_w} \ln \left(1 - \frac{R J_w}{J_w + k_s} \right) \]
IHSDM-FT

In a diffusion-based membrane process treating water with the capacity to form an accumulation of rejected solute near the membrane surface, permeate concentration can be predicted using the IHSDM-FT, shown as Equation 2-15. An example calculation is presented using the HSDM-FT on a single 1,4-dioxane pilot-scale experiment.

\[
C_P = \frac{k_s C_F}{-R J W e^{J W/k_b}} \ln \left(1 - \frac{R J W}{J W + k_s e^{J W/k_b}}\right)
\]

\[
C_P = \frac{3.92 \frac{ft}{d} \times 1.1 \times 10^{-8} \frac{lb}{ft^3}}{-0.846 \times 2.01 \frac{ft}{d}} \ln \left(1 - \frac{0.846 \frac{2.01 ft}{d}}{2.01 \frac{ft}{d} + 3.92 \frac{ft}{d}}\right) = 8.55 \times 10^{-9} \frac{lb}{ft^3} = 137 \frac{ng}{L}
\]

ERRSQ

The sum of the squared differences between the actual and theoretical concentrations is a measurement of error known as the sum square of errors (ERRSQ) shown as Equation 4-9, and is a widely used in adsorption isotherm modeling. An example error analysis calculation is performed on the Langmuir-modeled equilibrium concentration of R-ibuprofen, shown as Table B-1.

\[
ERRSQ = \sum_{i=1}^{n} (A - T)^2
\]
Table B-1: Example ERRSQ calculation

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Experimental qe (µg/cm²)</th>
<th>Calculated qe (µg/cm²)</th>
<th>ERRSQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.039</td>
<td>0.013</td>
<td>$(0.013 \frac{\mu g}{cm^2} - 0.039 \frac{\mu g}{cm^2})^2 = 6.68 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td>0.052</td>
<td>0.030</td>
<td>$(0.030 \frac{\mu g}{cm^2} - 0.052 \frac{\mu g}{cm^2})^2 = 4.82 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.043</td>
<td>0.020</td>
<td>$(0.020 \frac{\mu g}{cm^2} - 0.043 \frac{\mu g}{cm^2})^2 = 5.71 \times 10^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>0.019</td>
<td>0.004</td>
<td>$(0.004 \frac{\mu g}{cm^2} - 0.019 \frac{\mu g}{cm^2})^2 = 2.22 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>0.032</td>
<td>0.010</td>
<td>$(0.010 \frac{\mu g}{cm^2} - 0.032 \frac{\mu g}{cm^2})^2 = 5.02 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>0.042</td>
<td>0.014</td>
<td>$(0.014 \frac{\mu g}{cm^2} - 0.042 \frac{\mu g}{cm^2})^2 = 7.47 \times 10^{-4}$</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>$3.19 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**RPD**

RPD determines the percent difference between two numbers, shown as Equation 3-5, and is a measure of precision. An example RPD calculation is presented for duplicate feed concentration measurements for R-ibuprofen.

$$\% RPD = \frac{|S - D|}{S + D} \times 100$$

$$\% RPD = \frac{212.9 \frac{\mu g}{L} - 205.5 \frac{\mu g}{L}}{212.9 \frac{\mu g}{L} + 205.5 \frac{\mu g}{L}} \times 100 = 3.54$$
I-Stat

I-stat determines the difference between two numbers, shown as Equation 3-6, and is a measure of precision. An example I-stat calculation is presented for duplicate feed concentration measurements for R-ibuprofen.

\[
I - \text{stat} = \frac{|S - D|}{S + D}
\]  
(3-6)

\[
I - \text{stat} = \frac{212.9 \frac{\mu g}{L} - 205.5 \frac{\mu g}{L}}{212.9 \frac{\mu g}{L} + 205.5 \frac{\mu g}{L}} = 0.0177
\]

RMSE

The RMSE is a measurement of how far points are from a regression line, shown as Equation 4-10. An example RMSE calculation is conducted for the Langmuir-modeled equilibrium concentration of R-ibuprofen, shown as Table B-2.

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{n} (A - T)^2}{n}}
\]  
(4-10)
Table B-2: Example RMSE calculation

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Experimental qe (µg/cm²)</th>
<th>Calculated qe (µg/cm²)</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.039</td>
<td>0.013</td>
<td>((0.013 \frac{\mu g}{cm^2} - 0.039 \frac{\mu g}{cm^2})^2 = 6.68 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.052</td>
<td>0.030</td>
<td>((0.030 \frac{\mu g}{cm^2} - 0.052 \frac{\mu g}{cm^2})^2 = 4.82 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>0.043</td>
<td>0.020</td>
<td>((0.020 \frac{\mu g}{cm^2} - 0.043 \frac{\mu g}{cm^2})^2 = 5.71 \times 10^{-4})</td>
</tr>
<tr>
<td>4</td>
<td>0.019</td>
<td>0.004</td>
<td>((0.004 \frac{\mu g}{cm^2} - 0.019 \frac{\mu g}{cm^2})^2 = 2.22 \times 10^{-4})</td>
</tr>
<tr>
<td>5</td>
<td>0.032</td>
<td>0.010</td>
<td>((0.010 \frac{\mu g}{cm^2} - 0.032 \frac{\mu g}{cm^2})^2 = 5.02 \times 10^{-4})</td>
</tr>
<tr>
<td>6</td>
<td>0.042</td>
<td>0.014</td>
<td>((0.014 \frac{\mu g}{cm^2} - 0.042 \frac{\mu g}{cm^2})^2 = 7.47 \times 10^{-4})</td>
</tr>
</tbody>
</table>

\[\text{RMSE} = \sqrt{\frac{3.19 \times 10^{-3}}{6}} = 2.31 \times 10^{-2}\]

**t value**

The t-value measures the magnitude of difference in the variation of sample data. An example of the t-value calculation is completed for a comparison of experimental and HSDM-predicted R-ibuprofen permeate concentration, shown as Table B-3.

\[
t = \frac{x_{diff,\text{avg}}}{S_M}
\]

\[
S_M = \sqrt{\frac{\sum_{i=1}^{n}(x_{diff} - x_{diff,\text{ave}})^2}{n * df}}
\]
### Table B-3: Example t-value calculations

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Experimental R-ibuprofen permeate concentration (µg/L)</th>
<th>HSDM predicted R-ibuprofen permeate concentration (µg/L)</th>
<th>$X_{\text{diff}}$</th>
<th>$X_{\text{diff}} - X_{\text{diff,ave}}$</th>
<th>$(X_{\text{diff}} - X_{\text{diff,ave}})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>144.8</td>
<td>145.1</td>
<td>0.3</td>
<td>-4.14</td>
<td>17.2</td>
</tr>
<tr>
<td>2</td>
<td>60.2</td>
<td>67.6</td>
<td>7.41</td>
<td>2.96</td>
<td>8.75</td>
</tr>
<tr>
<td>3</td>
<td>256</td>
<td>291</td>
<td>35.4</td>
<td>31.1</td>
<td>961</td>
</tr>
<tr>
<td>4</td>
<td>50.3</td>
<td>50.8</td>
<td>0.5</td>
<td>-3.95</td>
<td>15.6</td>
</tr>
<tr>
<td>5</td>
<td>28.2</td>
<td>26.7</td>
<td>-1.51</td>
<td>-5.96</td>
<td>35.4</td>
</tr>
<tr>
<td>6</td>
<td>301</td>
<td>268</td>
<td>-32.4</td>
<td>-36.9</td>
<td>1360</td>
</tr>
<tr>
<td>7</td>
<td>410</td>
<td>432</td>
<td>-21.4</td>
<td>17.0</td>
<td>288</td>
</tr>
</tbody>
</table>

$X_{\text{diff,ave}}$: 4.45

Sum: 2690

$$S_M = \sqrt{\frac{2690}{7 \times 6}} = 8$$

$$t = \frac{4.45}{8} = 0.556$$
APPENDIX C. HSDM AND HSDM-FT MODEL DERIVATION
Using a definitive boundary and mass balance approach around a NF membrane element, equations can be determined and manipulated to derive the HSDM and HSDM-FT. Equations were previously mentioned in CHAPTER 2. The HSDM can be derived by following steps 1-12.

\[ Q_F = Q_P + Q_C \]  \hspace{1cm} (2-1)

\[ Q_F C_F = Q_P C_P + Q_C C_C \]  \hspace{1cm} (2-2)

\[ R = \left( \frac{Q_P}{Q_F} \right) \]  \hspace{1cm} (2-3)

\[ r = \frac{C_F - C_P}{C_F} \]  \hspace{1cm} (2-4)

\[ J_w = k_w(\Delta P - \Delta \pi) = \frac{Q_P}{A} \]  \hspace{1cm} (2-8)

\[ J_s = k_s(C_{FC} - C_P) = k_s \left[ \frac{C_F + C_C}{2} - C_P \right] = \frac{Q_P C_P}{A} \]  \hspace{1cm} (2-9)

\[ \frac{C_{FC} - C_P}{C_F - C_P} = \exp \left( \frac{J_w}{k_b} \right) \]  \hspace{1cm} (2-13)

Step 1. Rearrange Equation 2-1 for \( C_C \) and insert into Equation 2-2. Solve for \( C_F \).

\[ Q_C = Q_F - Q_P \]

\[ C_F = \frac{Q_P C_P + (Q_F - Q_P)C_C}{Q_F} \]

\[ C_F = \frac{Q_P C_P}{Q_F} + \frac{Q_F C_C}{Q_F} - \frac{Q_P C_C}{Q_F} \]

Step 2. Substitute \( (Q_P/Q_F) \) in for R.

\[ C_F = R C_P + C_C - R C_C \]  \hspace{1cm} (C-1)

Step 3. Equating Equations 2-8 and 2-9, and solving for \( (C_{FC} - C_P) \) yields:

\[ C_P J_w = k_s \left( \frac{C_F + C_C}{2} \right) - C_P \]
\[
\left(\frac{C_F + C_C}{2}\right) - C_P = \frac{C_P J_w}{k_s} \tag{C-2}
\]

Step 4. Solving for \( C_c \) simplifies to:

\[
\left(\frac{C_F + C_C}{2}\right) = \frac{C_P J_w}{k_s} + C_P
\]

\[
C_F + C_C = \frac{2C_P J_w}{k_s} + 2C_P
\]

\[
C_C = \frac{2C_P J_w}{k_s} + 2C_P - C_F \tag{C-3}
\]

Step 5. Inserting C-3 into C-1 yields:

\[
C_F = R C_P + \left(\frac{2C_P J_w}{k_s} + 2C_P - C_F\right) - R\left(\frac{2C_P J_w}{k_s} + 2C_P - C_F\right) \tag{C-4}
\]

Step 6. Expanding C-4 yields:

\[
C_F = R C_P + \frac{2C_P J_w}{k_s} + 2C_P - C_F - \frac{2R C_P J_w}{k_s} - 2R C_P + R C_F
\]

Step 7. Rearranging to group \( C_P \) and \( C_F \) equates to:

\[
C_F = C_F (R - 1) + C_P \left( R + \frac{2J_w R}{k_s} + 2 - \frac{2J_w R}{k_s} - 2R \right)
\]

\[
C_F - (C_F (R - 1)) = C_P \left( R + \frac{2J_w R}{k_s} + 2 - \frac{2J_w R}{k_s} - 2R \right)
\]

\[
C_F (2 - R) = C_P \left( R + \frac{2J_w}{k_s} + 2 - \frac{2J_w R}{k_s} - 2R \right)
\]

\[
C_F (2 - R) = C_P \left( \frac{2J_w}{k_s} - \frac{2J_w R}{k_s} + 2 - R \right)
\]

Step 8. Solving for \( C_P \) yields:

\[
C_P = \frac{C_F (2 - R)}{\left( \frac{2J_w}{k_s} - \frac{2J_w R}{k_s} + 2 - R \right)}
\]

Step 9. Factoring out \( \frac{J_w}{k_s} \) yields and rearranging:
\[ C_P = \frac{C_F (2 - R)}{\left( \frac{J_w}{k_s} (2 - 2R) + 2 - R \right)} \]

Step 10. Multiplying both sides of the equation by \( \frac{k_s}{k_s} \) produces:

\[ C_P = \frac{k_s C_F (2 - R)}{(J_w (2 - 2R) + k_s (2 - R))} \]

Step 11. Dividing both sides of the equation by \( \frac{2 - R}{2 - R} \) and simplifying yields:

\[ C_P = \frac{k_s C_F}{2 - R} \]

\[ C_P = \frac{k_s C_F}{J_w \left( \frac{2 - 2R}{2 - R} + k_s \right)} \]

Step 12. Substituting Equation 2-8 in for \( J_w \), the HSDM model is formed, previously displayed as Equation 2-11.

\[ C_P = \frac{k_s C_F}{k_w (\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s} \quad (2-11) \]

The HSDM can also be manipulated to predict rejection, if Equation 2-4 is solved for \( C_P \) and inserted into Equation 2-11.

\[ r = \frac{C_F - C_P}{C_F} \]

\[ rC_F = C_F - C_P \]

\[ rC_F - C_F = -C_P \]

\[ -rC_F + C_F = C_P \]

\[ C_P = C_F (1 - r) \]
\[ C_F(1 - r) = \frac{k_s C_F}{k_w (\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s} \quad \text{(C-5)} \]

Equation C-5 can be solved for \( r \), yielding a modified HSDM that can predict rejection of a solute:

\[ r = 1 - \frac{k_s}{k_w (\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s} \]

The HSDM model can be further manipulated to incorporate effects of concentration polarization on the surface of a membrane. Equation 2-13, which describes concentration polarization based on film theory can be solved for \( C_{FC} - C_p \).

\[ C_{FC} - C_p = (C_B - C_p) \exp \left( \frac{J_w}{k_B} \right) \quad \text{(C-6)} \]

\( C_B \) can be approximated as the arithmetic average of the feed and concentrate concentrations, and therefore Equation C-6 is inserted into Equation C-2 and solved for \( C_C \).

\[ \left( \frac{C_F + C_C}{2} \right) - C_p = \frac{C_p J_w}{k_s} \exp^{\frac{J_w}{k_B}} \]

\[ \left( \frac{C_F + C_C}{2} \right) = \frac{C_p J_w}{k_s \exp^{\frac{J_w}{k_B}}} + C_p \]

\[ C_F + C_C = \frac{2C_p J_w}{k_s \exp^{\frac{J_w}{k_B}}} + 2C_p \]
\[ C_C = \frac{2C_P J_w}{k_s \exp^{k_b}} + 2C_P - C_F \quad \text{(C-7)} \]

Equation C-7 is then inserted into Equation 1. Steps 6-12 are replicated for Equation C-7, yielding the HSDM-FT model, displayed as Equation 2-12.

\[ C_P = \frac{k_s C_F \exp \left( \frac{J_w}{k_b} \right)}{k_w (\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s \exp \left( \frac{J_w}{k_b} \right)} \quad \text{(2-12)} \]

The HSDM can also be manipulated to predict rejection, if Equation 2-4 is solved for \( C_P \) and inserted into Equation 2-12.

\[ r = 1 - \frac{k_s \exp \left( \frac{J_w}{k_b} \right)}{k_w (\Delta P - \Delta \pi) \left( \frac{2 - 2R}{2 - R} \right) + k_s \exp \left( \frac{J_w}{k_b} \right)} \]

Other models used in this work such as the IHSDM, IHSDM-FT, IOPM, and IOPM are based off the HSDM and HSDM-FT. Derivations for the aforementioned models can be found elsewhere (Mulford, 1999; Zhao, 2004).
APPENDIX D. MASS BALANCE CALCULATIONS
Feed, permeate, and concentrate samples were collected for enantiomeric ibuprofen and 1,4-dioxane experiments to perform mass balance calculations. Mass balance calculations authenticate experimental procedures and verify mass is accounted for in each stream. Mass balance equations were solved for theoretical concentrate concentration and compared to the actual stream’s content. Equation 2-2 can be rearranged to solve for theoretical concentrate concentration, shown as Equation D-1.

Equation 2-2:

\[ Q_F = Q_P + Q_C \]  

\[ Q_F C_F = Q_P C_P + Q_C C_C \]  

\[ \frac{Q_F C_F - Q_P C_P}{Q_C} = C_C \]  

RDP is used to compare the theoretical and actual concentrate calculations. Equation 3-5 was modified to present a comparison between an experimental concentrate concentration and empirically calculated amount, shown as D-2. RPD is generally acceptable if the value is less or equal to ten percent.

\[ RPD = \frac{|C_a - C_t|}{\frac{C_a + C_t}{2}} \times 100 \]  

Where,

\( C_a \) = actual sample concentration (mg/L)

\( C_t \) = theoretical sample concentration from mass balance (mg/L)
Table D-1 and Table D-2 present NF270 concentrate concentration mass balance calculations for R- and S- ibuprofen, respectively. The RPD was acceptable for 14 out of the 15 total experiments. Table D-3 and Table D-4 present TS40 concentrate concentration mass balance calculations for R- and S- ibuprofen respectively. The RPD was acceptable for 9 out of the 10 total experiments. It is important to note that the average feed value collected at time 24 h was used to calculate the theoretical concentrate concentration, as 0 h feed sample does not account for effects due to adsorption on the membrane or equipment. Results regarding ibuprofen adsorption onto equipment and membrane components are displayed in CHAPTER 4. Flow rates were individually collected and inserted into corresponding mass balance calculations. The feed flow rate was set to 1 L/min, permeate flow rate was based on feed pressure, membrane coupon, and water matrix type, and concentrate flow rate was determined by Equation 2-2.
Table D-1: NF270 R-ibuprofen 24 h concentrate mass balance RPD

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>24 h Feed Concentration (µg/L)</th>
<th>Permeate Concentration (µg/L)</th>
<th>Actual Concentrate Concentration (µg/L)</th>
<th>Theoretical Concentrate Concentration (µg/L)</th>
<th>RPD (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.5</td>
<td>28.2</td>
<td>36.1</td>
<td>32.7</td>
<td>9.85</td>
</tr>
<tr>
<td>2</td>
<td>64.8</td>
<td>48.6</td>
<td>68.3</td>
<td>65.2</td>
<td>4.71</td>
</tr>
<tr>
<td>3</td>
<td>72.8</td>
<td>60.2</td>
<td>74.5</td>
<td>72.9</td>
<td>2.27</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>145</td>
<td>167</td>
<td>171</td>
<td>2.40</td>
</tr>
<tr>
<td>5</td>
<td>338</td>
<td>283</td>
<td>364</td>
<td>340</td>
<td>6.76</td>
</tr>
<tr>
<td>6</td>
<td>349</td>
<td>256</td>
<td>336</td>
<td>351</td>
<td>4.21</td>
</tr>
<tr>
<td>7</td>
<td>517</td>
<td>410</td>
<td>529</td>
<td>519</td>
<td>1.81</td>
</tr>
<tr>
<td>8</td>
<td>624</td>
<td>476</td>
<td>610</td>
<td>624</td>
<td>2.27</td>
</tr>
<tr>
<td>9</td>
<td>570</td>
<td>225</td>
<td>608</td>
<td>570</td>
<td>6.38</td>
</tr>
<tr>
<td>10</td>
<td>652</td>
<td>474</td>
<td>712</td>
<td>652</td>
<td>8.74</td>
</tr>
<tr>
<td>11</td>
<td>528</td>
<td>404</td>
<td>487</td>
<td>528</td>
<td>7.94</td>
</tr>
<tr>
<td>12</td>
<td>120</td>
<td>102</td>
<td>138</td>
<td>120</td>
<td>14.0</td>
</tr>
<tr>
<td>13</td>
<td>254</td>
<td>232</td>
<td>266</td>
<td>254</td>
<td>4.76</td>
</tr>
<tr>
<td>14</td>
<td>396</td>
<td>331</td>
<td>360</td>
<td>397</td>
<td>9.66</td>
</tr>
<tr>
<td>15</td>
<td>930</td>
<td>871</td>
<td>890</td>
<td>930</td>
<td>4.39</td>
</tr>
</tbody>
</table>
Table D-2: NF270 S-ibuprofen 24 h concentrate mass balance RPD

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>24 h Feed Concentration (µg/L)</th>
<th>Permeate Concentration (µg/L)</th>
<th>Actual Concentrate Concentration (µg/L)</th>
<th>Theoretical Concentrate Concentration (µg/L)</th>
<th>RPD (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.1</td>
<td>16.9</td>
<td>24.9</td>
<td>23.3</td>
<td>6.69</td>
</tr>
<tr>
<td>2</td>
<td>46.1</td>
<td>36.3</td>
<td>49.2</td>
<td>46.3</td>
<td>6.10</td>
</tr>
<tr>
<td>3</td>
<td>54.0</td>
<td>40.5</td>
<td>54.0</td>
<td>53.9</td>
<td>0.167</td>
</tr>
<tr>
<td>4</td>
<td>139</td>
<td>107</td>
<td>151</td>
<td>140</td>
<td>7.43</td>
</tr>
<tr>
<td>5</td>
<td>310</td>
<td>245</td>
<td>315</td>
<td>313</td>
<td>0.800</td>
</tr>
<tr>
<td>6</td>
<td>321</td>
<td>237</td>
<td>305</td>
<td>324</td>
<td>5.85</td>
</tr>
<tr>
<td>7</td>
<td>488</td>
<td>366</td>
<td>474</td>
<td>491</td>
<td>3.56</td>
</tr>
<tr>
<td>8</td>
<td>593</td>
<td>420</td>
<td>542</td>
<td>593</td>
<td>8.92</td>
</tr>
<tr>
<td>9</td>
<td>536</td>
<td>182</td>
<td>498</td>
<td>536</td>
<td>7.26</td>
</tr>
<tr>
<td>10</td>
<td>622</td>
<td>407</td>
<td>625</td>
<td>621</td>
<td>0.665</td>
</tr>
<tr>
<td>11</td>
<td>492</td>
<td>362</td>
<td>474</td>
<td>492</td>
<td>3.73</td>
</tr>
<tr>
<td>12</td>
<td>74.5</td>
<td>58.1</td>
<td>86.4</td>
<td>74.6</td>
<td>12.6</td>
</tr>
<tr>
<td>13</td>
<td>196</td>
<td>169</td>
<td>200</td>
<td>196</td>
<td>2.16</td>
</tr>
<tr>
<td>14</td>
<td>331</td>
<td>267</td>
<td>320</td>
<td>331</td>
<td>3.25</td>
</tr>
<tr>
<td>15</td>
<td>844</td>
<td>772</td>
<td>805</td>
<td>844</td>
<td>4.76</td>
</tr>
</tbody>
</table>
### Table D-3: TS40 R-ibuprofen 24 h concentrate mass balance RPD

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>24 h Feed Concentration (µg/L)</th>
<th>Permeate Concentration (µg/L)</th>
<th>Actual Concentrate Concentration (µg/L)</th>
<th>Theoretical Concentrate Concentration (µg/L)</th>
<th>RPD (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.6</td>
<td>12.7</td>
<td>42.7</td>
<td>43.1</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td>63.7</td>
<td>17.9</td>
<td>57.4</td>
<td>65.0</td>
<td>12.5</td>
</tr>
<tr>
<td>3</td>
<td>85.6</td>
<td>34.8</td>
<td>79.2</td>
<td>86.9</td>
<td>9.27</td>
</tr>
<tr>
<td>4</td>
<td>171</td>
<td>111</td>
<td>163</td>
<td>172</td>
<td>5.44</td>
</tr>
<tr>
<td>5</td>
<td>233</td>
<td>143</td>
<td>220</td>
<td>234</td>
<td>6.13</td>
</tr>
<tr>
<td>6</td>
<td>393</td>
<td>260</td>
<td>416</td>
<td>393</td>
<td>5.79</td>
</tr>
<tr>
<td>7</td>
<td>618</td>
<td>245</td>
<td>614</td>
<td>619</td>
<td>0.718</td>
</tr>
<tr>
<td>8</td>
<td>670</td>
<td>189</td>
<td>666</td>
<td>670</td>
<td>0.590</td>
</tr>
<tr>
<td>9</td>
<td>621</td>
<td>169</td>
<td>671</td>
<td>622</td>
<td>7.63</td>
</tr>
<tr>
<td>10</td>
<td>419</td>
<td>289</td>
<td>487</td>
<td>419</td>
<td>5.35</td>
</tr>
</tbody>
</table>

### Table D-4: TS40 S-ibuprofen 24 h concentrate mass balance RPD

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>24 h Feed Concentration (µg/L)</th>
<th>Permeate Concentration (µg/L)</th>
<th>Actual Concentrate Concentration (µg/L)</th>
<th>Theoretical Concentrate Concentration (µg/L)</th>
<th>RPD (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.1</td>
<td>10.1</td>
<td>33.7</td>
<td>31.5</td>
<td>6.72</td>
</tr>
<tr>
<td>2</td>
<td>53.5</td>
<td>17.2</td>
<td>50.9</td>
<td>54.5</td>
<td>6.89</td>
</tr>
<tr>
<td>3</td>
<td>79.7</td>
<td>32.4</td>
<td>75.3</td>
<td>80.9</td>
<td>7.12</td>
</tr>
<tr>
<td>4</td>
<td>137</td>
<td>77.3</td>
<td>141</td>
<td>138</td>
<td>1.84</td>
</tr>
<tr>
<td>5</td>
<td>196</td>
<td>124</td>
<td>195</td>
<td>198</td>
<td>1.30</td>
</tr>
<tr>
<td>6</td>
<td>352</td>
<td>198</td>
<td>321</td>
<td>352</td>
<td>9.19</td>
</tr>
<tr>
<td>7</td>
<td>560</td>
<td>215</td>
<td>547</td>
<td>561</td>
<td>2.41</td>
</tr>
<tr>
<td>8</td>
<td>607</td>
<td>148</td>
<td>535</td>
<td>607</td>
<td>12.7</td>
</tr>
<tr>
<td>9</td>
<td>604</td>
<td>133</td>
<td>553</td>
<td>604</td>
<td>8.77</td>
</tr>
<tr>
<td>10</td>
<td>385</td>
<td>248</td>
<td>370</td>
<td>385</td>
<td>4.10</td>
</tr>
</tbody>
</table>
Table D-5 presents the concentrate mass balance RPD values for the eight pilot-scale 1,4-dioxane experiments conducted. NF pilot unit flow rates are usually consistent, therefore constant flow rates were used in the mass balance calculations. Two experiments are out of the generally acceptable RPD range. Reasons that could explain the inconsistencies include deviant flow rates, contaminated concentrate sample bottle, or adsorption of 1,4-dioxane onto the equipment or membrane surface. However, an independent experiment conducted found less than 5 percent adsorption of 1,4-dioxane onto a membrane surface or membrane equipment, therefore rejecting that hypothesis.

Table D-5: 1,4-Dioxane concentrate mass balance RPD

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>Feed concentration (ng/L)</th>
<th>Permeate concentration (ng/L)</th>
<th>Actual concentrate concentration (ng/L)</th>
<th>Theoretical concentrate concentration (ng/L)</th>
<th>RPD (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>150</td>
<td>320</td>
<td>341</td>
<td>6.48</td>
</tr>
<tr>
<td>2</td>
<td>760</td>
<td>660</td>
<td>1200</td>
<td>1300</td>
<td>7.85</td>
</tr>
<tr>
<td>3</td>
<td>890</td>
<td>770</td>
<td>1600</td>
<td>1,660</td>
<td>3.88</td>
</tr>
<tr>
<td>4</td>
<td>6,200</td>
<td>5,700</td>
<td>7,600</td>
<td>8,890</td>
<td>15.6</td>
</tr>
<tr>
<td>5</td>
<td>15,800</td>
<td>15,000</td>
<td>18,700</td>
<td>20,100</td>
<td>7.24</td>
</tr>
<tr>
<td>6</td>
<td>27,000</td>
<td>24,000</td>
<td>50,000</td>
<td>43,100</td>
<td>14.7</td>
</tr>
<tr>
<td>7</td>
<td>37,600</td>
<td>33,000</td>
<td>57,300</td>
<td>62,300</td>
<td>8.44</td>
</tr>
<tr>
<td>8</td>
<td>38,400</td>
<td>33,000</td>
<td>62,600</td>
<td>67,500</td>
<td>7.46</td>
</tr>
</tbody>
</table>

Note: $Q_F = 267$ gal/min, $Q_P = 226$ gal/min, $Q_C = 42$ gal/min
APPENDIX E. QUALITY CONTROL
Quality control measures were conducted in accordance with Standard Methods, described in CHAPTER 3, and presented herein. Data sets were analyzed for accuracy and precision. Samples were spiked, analyzed for SPE recovery, and plotted on an accuracy control chart. Accuracy control charts for R- and S- ibuprofen are displayed in Figure E-1 and Figure E-2, respectively. Samples were also duplicated, analyzed for relative percent difference, and plotted on a precision control chart. Precision control charts for R- and S- ibuprofen are displayed in Figure E-3 to Figure E-4, and Figure E-5 to Figure E-6, respectively. Duplicates for 1,4-dioxane are listed in Table E-1.

Accuracy Charts

![Accuracy Chart](image)

Figure E-1: R-ibuprofen spike control chart
Figure E-2: S-ibuprofen spike control chart

Precision Charts

Figure E-3: R-ibuprofen duplicate RPD control chart
Figure E-4: S-ibuprofen duplicate RPD control chart

Figure E-5: R-ibuprofen duplicate I-stat control chart
Table E-1: 1,4-Dioxane RPD and I-stat

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Sample</th>
<th>Sample concentration (ng/L)</th>
<th>Sample duplicate concentration (ng/L)</th>
<th>RPD (percent)</th>
<th>I-stat</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Feed</td>
<td>180</td>
<td>180</td>
<td>0.00</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>Feed</td>
<td>890</td>
<td>910</td>
<td>2.22</td>
<td>0.011</td>
</tr>
<tr>
<td>4</td>
<td>Feed</td>
<td>6,200</td>
<td>6,100</td>
<td>1.63</td>
<td>0.008</td>
</tr>
<tr>
<td>6</td>
<td>Feed</td>
<td>27,000</td>
<td>28,000</td>
<td>3.64</td>
<td>0.018</td>
</tr>
<tr>
<td>7</td>
<td>Feed</td>
<td>37,600</td>
<td>36,000</td>
<td>4.35</td>
<td>0.022</td>
</tr>
<tr>
<td>8</td>
<td>Feed</td>
<td>38,400</td>
<td>38,200</td>
<td>0.522</td>
<td>0.003</td>
</tr>
</tbody>
</table>
APPENDIX F. ADSORPTION ISOTHERM MODELS
Langmuir, Freundlich, and Temkin isotherms were utilized to model the adsorption of R-and S-ibuprofen onto the membrane equipment with and without a membrane coupon installed. Linearized isotherm plots for R- and S- ibuprofen are displayed in this section, where the derived model constants and associated parameters are presented in CHAPTER 4.

Figure F-1: Linearized Langmuir R- and S- ibuprofen isotherm plot of flat-sheet equipment

Figure F-2: Linearized Freundlich R- and S- ibuprofen isotherm plot of flat-sheet equipment
Figure F-3: Linearized Temkin R- and S-ibuprofen isotherm plot of flat-sheet equipment

\[ y = 0.011x - 0.020 \quad R^2 = 0.9743 \]
\[ y = 0.007x - 0.022 \quad R^2 = 0.981 \]

Figure F-4: Linearized Langmuir R- and S-ibuprofen isotherm plot of NF270 membrane in operation

\[ y = 7510x + 30.6 \quad R^2 = 0.995 \]
\[ y = 1220x + 17.6 \quad R^2 = 0.982 \]
Figure F-5: Linearized Freundlich R- and S- ibuprofen isotherm plot of NF270 membrane in operation

Figure F-6: Linearized Temkin R- and S- ibuprofen isotherm plot of NF270 membrane in operation
Figure F-7: Linearized Langmuir R- and S-ibuprofen isotherm plot of TS40 membrane in operation

Figure F-8: Linearized Freundlich R- and S-ibuprofen isotherm plot of TS40 membrane in operation
Figure F-9: Linearized Temkin R- and S-ibuprofen isotherm plot of TS40 membrane in operation

\[
y = 0.020x - 0.057 \\
R^2 = 0.975
\]

\[
y = 0.009x - 0.030 \\
R^2 = 0.963
\]

Figure F-10: Linearized Langmuir R- and S-ibuprofen isotherm plot of NF270 membrane in high-pressure operation

\[
y = 1909x + 10.6 \\
R^2 = 0.981
\]

\[
y = 367x + 6.73 \\
R^2 = 0.976
\]
Figure F-11: Linearized Freundlich R- and S- ibuprofen isotherm plot of NF270 membrane in high-pressure operation

Figure F-12: Linearized Temkin R- and S- ibuprofen isotherm plot of NF270 membrane in high-pressure operation
APPENDIX G. REGRESSION MODEL DERIVATION USING MICROSOFT EXCEL
To create a model that can predict the overestimation ibuprofen rejection based on sample time, experimental data from this study was inserted into the regression tool of Microsoft Excel®. Parameters known to influence ibuprofen rejection include initial concentration, adsorbed contents, feed water pH, and permeate flux and hence were used in the model. Detailed experimental data inserted into the regression software is displayed in Table G-1. Output parameters and statistical analysis for the data set is presented in Table G-2 to Table G-5.

Table G-1: Input parameters in model derivation

<table>
<thead>
<tr>
<th>X (dependent) variables</th>
<th>Y (independent) variable</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C₀ (µg/L)</strong></td>
<td><strong>C₀-Cᵉ (µg/L)</strong></td>
</tr>
<tr>
<td>74.6</td>
<td>17.7</td>
</tr>
<tr>
<td>139</td>
<td>27.9</td>
</tr>
<tr>
<td>161</td>
<td>34.3</td>
</tr>
<tr>
<td>384</td>
<td>51.3</td>
</tr>
<tr>
<td>720</td>
<td>68.4</td>
</tr>
<tr>
<td>741</td>
<td>70.9</td>
</tr>
<tr>
<td>1080</td>
<td>83.7</td>
</tr>
<tr>
<td>1280</td>
<td>57.7</td>
</tr>
<tr>
<td>1150</td>
<td>41.5</td>
</tr>
<tr>
<td>324</td>
<td>129</td>
</tr>
<tr>
<td>620</td>
<td>170</td>
</tr>
<tr>
<td>921</td>
<td>193</td>
</tr>
<tr>
<td>2010</td>
<td>228</td>
</tr>
<tr>
<td>Table G-2: Parameters obtained from regression analysis</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Coefficients</strong></td>
<td><strong>Standard Error</strong></td>
</tr>
<tr>
<td>Intercept</td>
<td>-4.32</td>
</tr>
<tr>
<td>$C_o$</td>
<td>0.014</td>
</tr>
<tr>
<td>$C_o$-$C_e$</td>
<td>-0.069</td>
</tr>
<tr>
<td>$R_{ini}$</td>
<td>0.937</td>
</tr>
<tr>
<td>pH</td>
<td>-0.081</td>
</tr>
<tr>
<td>$J_w$</td>
<td>-0.247</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table G-3: Regression statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Multiple R</td>
</tr>
<tr>
<td>R$^2$</td>
</tr>
<tr>
<td>Adjusted R$^2$</td>
</tr>
<tr>
<td>Standard Error</td>
</tr>
<tr>
<td>Observations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table G-4: Analysis of variance (ANOVA) statistical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>df</strong></td>
</tr>
<tr>
<td>Regression</td>
</tr>
<tr>
<td>Residual</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

NF270 curated rejection values of ibuprofen from independent literature with associated operational parameters were inserted into the predictive model, yielding quasi-equilibrated removal. Adsorbed ibuprofen concentration ($C_o$-$C_e$) values from outside literature sources were approximated based from experimental data of this study.
Table G-5: Equilibrated ibuprofen rejection of intendent literature based on predictive model

<table>
<thead>
<tr>
<th>$C_o$ (µg/L)</th>
<th>$C_o-C_e$ (µg/L)</th>
<th>pH</th>
<th>$J_w$ (gal/ft²d)</th>
<th>$R_{ini}$ (percent)</th>
<th>$R_{equ}$ (percent)</th>
<th>R Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>66.2</td>
<td>3.5</td>
<td>31.8</td>
<td>85</td>
<td>69.7</td>
<td>18.0</td>
</tr>
<tr>
<td>500</td>
<td>56.2</td>
<td>4.5</td>
<td>31.8</td>
<td>89</td>
<td>74.0</td>
<td>16.8</td>
</tr>
<tr>
<td>500</td>
<td>47.7</td>
<td>5.5</td>
<td>31.8</td>
<td>87</td>
<td>72.7</td>
<td>16.5</td>
</tr>
<tr>
<td>750</td>
<td>71.0</td>
<td>4.0</td>
<td>31.8</td>
<td>90</td>
<td>77.5</td>
<td>13.8</td>
</tr>
<tr>
<td>750</td>
<td>50.2</td>
<td>5.0</td>
<td>31.8</td>
<td>89</td>
<td>78.0</td>
<td>12.4</td>
</tr>
<tr>
<td>750</td>
<td>31.5</td>
<td>6.0</td>
<td>31.8</td>
<td>94</td>
<td>83.9</td>
<td>10.8</td>
</tr>
<tr>
<td>750</td>
<td>71.0</td>
<td>4.0</td>
<td>31.8</td>
<td>83</td>
<td>71.0</td>
<td>14.5</td>
</tr>
<tr>
<td>750</td>
<td>50.2</td>
<td>5.0</td>
<td>31.8</td>
<td>85</td>
<td>74.2</td>
<td>12.7</td>
</tr>
<tr>
<td>750</td>
<td>31.5</td>
<td>6.0</td>
<td>31.8</td>
<td>92</td>
<td>82.0</td>
<td>10.9</td>
</tr>
<tr>
<td>200</td>
<td>44.1</td>
<td>3.5</td>
<td>45.3</td>
<td>12</td>
<td>5.26</td>
<td>56.2</td>
</tr>
<tr>
<td>200</td>
<td>34.1</td>
<td>4.5</td>
<td>45.3</td>
<td>44</td>
<td>25.8</td>
<td>41.3</td>
</tr>
<tr>
<td>200</td>
<td>29.1</td>
<td>5.5</td>
<td>45.3</td>
<td>86</td>
<td>65.4</td>
<td>23.9</td>
</tr>
</tbody>
</table>
REFERENCES


Higgins, C. J. & Duranceau, S. J. (2020). Modeling the mass transfer of 1,4-dioxane in a nanofiltration membrane process. *Desalination & Water Treatment, 191*, 1-10


Son, H., Im, J., & Zoh, K. (2009). A fenton-like degradation mechanism for 1,4-dioxane using zero-valent iron (Fe0) and UV light. *Water Research, 43*(5), 147-163.


U.S. Environmental Protection Agency. (2010). *Toxicological review of 1,4-dioxane* U.S. Environmental Protection Agency. Washington, DC, EPA/635/R-09/005F


