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by

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THESIS

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B.S., Civil Engineering, University of New Mexico, 2014
M.S., Civil Engineering, University of New Mexico, 2017

ABSTRACT

Factors such as increasing population, urbanization, and climate change have made the management of water resources a challenge for many municipalities. Water reuse, especially direct potable reuse (DPR) of treated wastewater, is increasingly seen as a potential source of water for communities facing water shortages. Due to improvements in analytical capabilities as well as concerns regarding toxicology of contaminants of emerging concern (CECs), the need for investigating the removal of CECs has become crucial for further DPR considerations. Reverse osmosis (RO) has been demonstrated to remove many CECs. Many studies, however, have investigated the removal of well-known CECs, often with high molecular weights and complex structures. This bench scale study investigated the rejection of low molecular weight compounds by RO membranes to correlate removal to molecular characteristics and physical properties. The data collected from experiments is also used to create a model to predict the CECs rejection between membranes used in experiments, utilizing boron as a reference between membrane products.

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1. Introduction

Factors such as increasing population, urbanization, and climate change have made the management of water resources a challenge for many municipalities. Water reuse is increasingly seen as a viable non-traditional source of water for communities facing drought, water scarcity, and increased demand for a growing population (Gerrity et al., 2013, Tchobanoglous et al., 2015). Desalination of seawater is also seen as an option for many of these communities located along a coast. Due to improvements in analytical capabilities as well as increased concern regarding the toxicology of contaminants of emerging concern, the need to document the removal of these constituents is important to support future direct potable reuse (DPR) projects. Furthermore, many neutral and low molecular weight compounds, such as boron, are difficult to remove with current treatment technologies, such as reverse osmosis (Mane et al., 2009).

Reverse osmosis (RO) is currently used for both water reuse and desalination. RO has been demonstrated to provide a high degree of removal of many large organic compounds, such as pharmaceuticals, but poor removal occurs for many compounds (Yoon et al., 2005). RO removal efficiency is affected by many factors, including the physical-chemical properties of the compound, membrane properties, process operating conditions, and feed water characteristics (Bellona et al., 2004). This research investigated the rejection of neutral organics and boron by RO membranes in a series of laboratory-scale experiments. The results allowed development of a relationship between the organics and boron removal using one ultra-low pressure and six reverse osmosis membrane products and organics. By comparing the mass transfer coefficient of the solute boron (k_{Boron}) through the membranes to the various mass transfer coefficients of the organics ($k_{Organics}$), a correlation was developed to predict the rejection of organics through other membrane products when the boron rejection is known.

1.1 Organic Compounds

Generally, RO membranes provide poor rejection of uncharged low molecular weight organics (Bellona et al., 2004). A few molecular properties have been used as general guidelines to understand the rejection of certain organic compounds through NF and RO membranes (Bellona et al., 2004). Various size parameters, charge, and several parameters characterizing the adsorption to the membrane surface have been investigated.

Many different size parameters have been investigated to understand the rejection of organic molecules by RO and NF membranes. Molecular weight has historically been the generally accepted size parameter in industry used to explain rejection, however, does not consider the geometry or shape of a molecule (Bellona et al., 2004). Many other molecule size properties addressing size exclusion as a means of organics rejection have been investigated. The solute radius was suggested to be a better parameter than molecular weight in predicting the rejection of small, uncharged organic compounds by Yoon et al. (2005). Stokes diameter, equivalent molar diameter, and calculated molecular diameter were investigated as size parameters in Van der Bruggen et al. (1999). All of the size parameters were found to have good correlations with rejection of the organic compounds tested. RO membranes gave better rejection for larger molecules. molecular width, length, depth, and volume are other size descriptors that have been investigated to understand how size of organic compounds affects rejection through RO membranes (Kiso et al., 2001, Comerton et al., 2008, Drewes et al., 2013, Sadmani et al., 2014, Jeffery-Black et al., 2016).

Charge plays an important role in rejection of solutes through RO membranes. Generally, thin film composite membranes have a slight negative charge to increase salt rejection and minimize fouling (Bellona et al., 2004, Yoon et al., 2005). Charge of the membrane and solutes are dependent on the feed water chemistry, including pH and solute concentrations. It is understood that charged organics experience better rejection than neutral organic compounds, with the main rejection mechanism being electrostatic repulsion for charged compounds (Yoon et al., 2005). None of the organics used in this study contain a charge at the feed pH chosen for experiments.

Two molecular properties investigated for describing organic interaction with the membrane material are polarizability and the octanol-water partitioning coefficient. Polarizability describes how easily electrons can move within a compound, or more specifically how easily a molecular electron cloud can be distorted due to an outside force (Drewes et al., 2013, Jeffery-Black et al., 2016). The study conducted by Jeffery-Black et al. (2016) looked at the rejection of 9 different organic compounds through a nanofiltration pilot unit utilizing the NF270 membrane. Polarizability was found to have an increasing linear trend with increasing rejection, having an R^2 value of 0.71 with rejection of the organics chosen (Jeffery-Black et al., 2016).

The octanol-water partitioning coefficient, or log K_{ow}, was investigated and found to correlate with rejection of organics (Bellona et al., 2004). The log K_{ow} describes the hydrophobicity of a molecule, where a low log K_{ow} value corresponds to a hydrophilic organic compound. The log K_{ow} has been used to describe an organic's ability to be rejected by the extent of the organic partitioning onto the membrane. Studies have shown that as log K_{ow} increases, rejection also increases (Van Der Bruggen et al., 2002, Drewes et al., 2006, Jeffery-Black et al., 2016).

In previous studies of organics removal by RO membranes, the organic compounds used in experiments were chosen based on its use by the industry, concern to public health, or to gain a wide range of the molecular property being tested to explain rejection (Libotean et al., 2008, Yoon et al., 2005, Kimura et al., 2004, Van der Bruggen et al., 1999, Sadmani et al., 2014, Kimura et al., 2003, Jeffery-Black et al., 2016). In this study, organic compounds were chosen so that the influence of individual functional groups on removal could be investigated, and a more mechanistic approach could be used to determine the rejection of which type of organic compounds correlates well with boron rejection.

1.2 Boron

Boron is abundant in many natural systems, as well as municipal wastewater. It is used in many products globally, including manufacturing of glass and ceramics, as well as detergents and bleaches (Woods, 1994). The average boron concentration in seawater is 4.5 mg/kg (WHO, 2004). While boron is essential to plant life, it can also be toxic to them at high levels (Woods, 1994). This has sparked recent public concern in states like California, where desalinated seawater and reuse water is being considered as a potential water source for many communities. The state of California set a notification level of boron to be 1,000 μg/L in drinking water (Marshack et al., 2016). A notification level based on the health based advisory level for chemicals for which maximum contaminant levels have not been established.

In water boron is most often present as neutral boric acid (H_3BO_3), which has a pKa of 9.2 (WHO, 2009). It has a small molecular weight of 61.83 g/mol. These two properties of boron make it difficult to remove by reverse osmosis treatment, with removal being highly dependent on the RO operating conditions (Hyung et al., 2006). Membrane manufacturers have started to include boron rejection on the specification sheets of their products, mainly for seawater RO membranes, due to the concern of toxicity to certain plants.

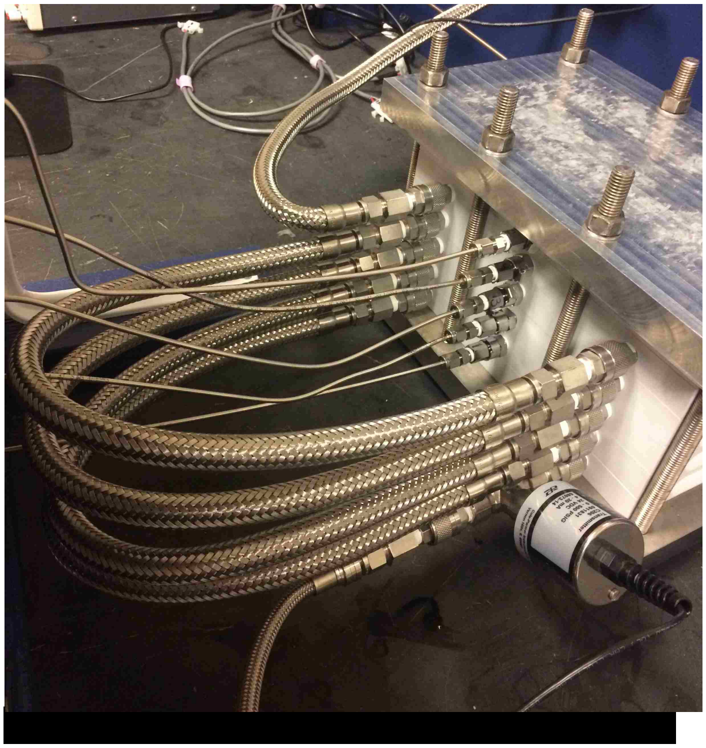
Increased concern for boron in treated water leads to the need to investigate boron rejection with different reverse osmosis membrane products. Furthermore, boron rejection has been correlated to the removal of other harmful organic compounds, such as N-nitrosodimethylamine (NDMA) rejection (Tu et al., 2013). NDMA is difficult to analyze, resulting in the need for a surrogate compound to be explored (Tu et al., 2013). Boron is easier to measure than most of organic compounds of concern, and is a non-volatile compound. Being able to correlate boron rejection with organics rejection would be beneficial to the water treatment industry. A correlation between boron removal and that of organic constituents would aid utilities both in selecting RO membranes for their treatment plants and in monitoring process performance.

2. Methods and Materials

Three experiments were completed using a bench-scale reverse osmosis system. Three different groups of membranes were used in the experiments: ultra-low pressure (ULP), brackish water (BW), and sea water (SW) membranes. These three experiments were done at different feed pressures based on the membranes being tested. Each of the three tests consisted of three phases. Phase one of the experiments was a cleaning and compaction with deionized water (DI), lasting 24 hours. The rejection of NaCl and boron was determined in the second phase of each experiment. The third phase of experiments focused on determining the rejection of a suite of low molecular weight organic compounds. More detailed explanation of how each test was completed is described below.

2.1 Experimental Apparatus

The RO membrane testing system, shown in Figure 2.1, is a custom-designed polypropylene flat-sheet membrane cell that can contain 5 separate sheets of membrane material, each with a membrane area of 0.016 m^2. The membrane cells are tested in series, meaning the feed water leaves the stainless steel feed tank, enters the first membrane, where the concentrate of the first membrane becomes the feed for the second membrane. This process continues through all 5 membranes. The use of this unique cell allows 5 membranes to be tested with the same feed solution simultaneously, significantly increasing the number of experiments that can be performed and the number of parameters that can be measured in each experiment. Viton O-rings were used in the membrane system, and all tubing used in the system is 316-stainless steel. A Wanner Hydra-Cell D03 positive displacement pump with variable speed drive fed the membrane cells. The water was maintained at constant temperature by a Thermo Neslab temperature controller. Pressure, temperature, and permeate flow rate were measured with on-line instruments monitored by a DATAQ DI-808 data acquisition system. Each instrument was calibrated before any experiments were conducted, with the largest percent of full-scale error being -2.50% for the permeate pressure transducer. Appendix A contains the full calibration report.



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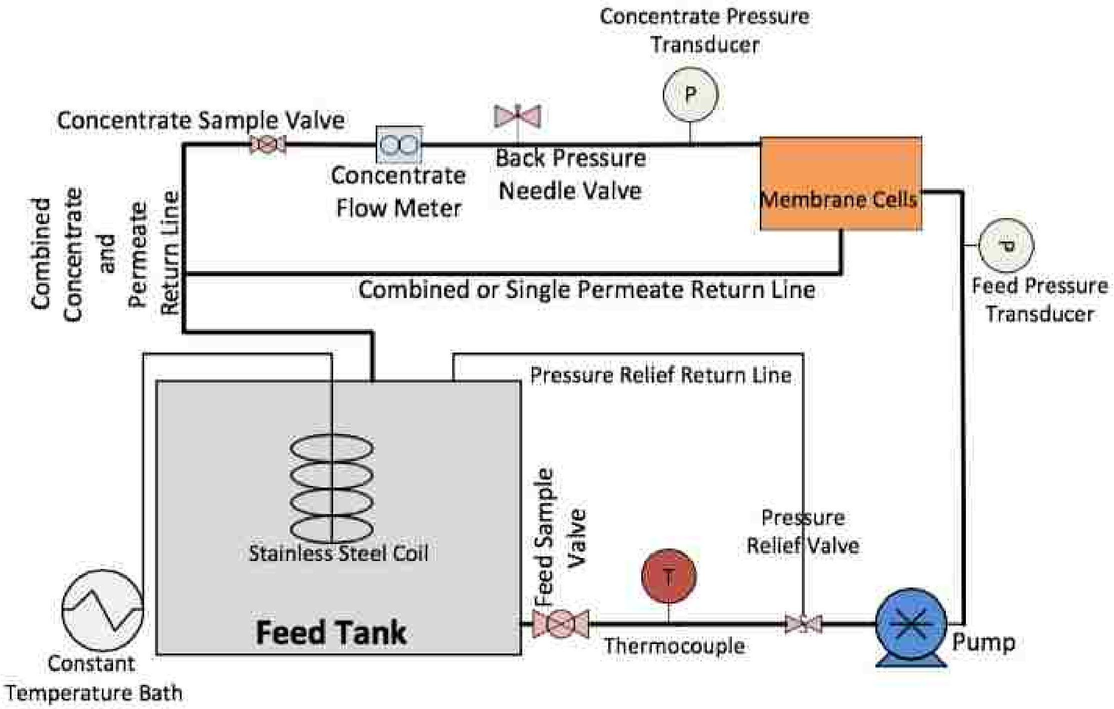
The permeate and concentrate were recycled to the stainless steel feed tank, except during sampling times. The permeate samples were collected one at a time by switching permeate flow from a combined stream to a single permeate flow stream, where a flow meter followed by a sample valve was located. This allowed the flow, and therefore the flux, to be measured through one permeate channel at a time during sampling. Figure 2.2 and Figure 2.3 show the experimental setup.



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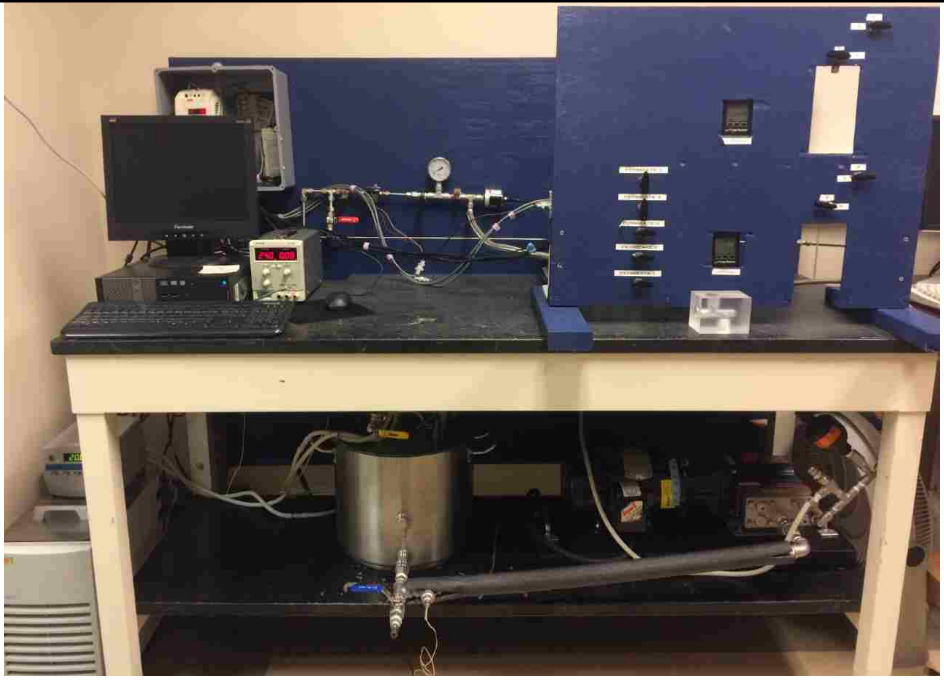

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After performing a mass balance to find the feed concentration for each individual membrane, it was found that the feed concentration changes very little from membrane to membrane. Furthermore, the recovery from each individual membrane is small, which leads to a reasonable conclusion that the corrected feed concentration for each membrane through the mass balance analysis can be used.

2.2 Membrane Products

Membrane material was provided by four membrane manufacturers. As mentioned above, three types of RO membrane products were tested. These include the ULP, BW, and SW membranes. The membranes used in all experiments are located in Table 2.1. These membranes were chosen to evaluate a variety of solute and water mass transfer coefficients. Each membrane group was tested at three different pressures. These three pressures were chosen based on the operating pressure for each membrane identified on the specification sheet, which are presented in Table 2.2.

Table 2.1: Membrane products and specification sheet information

		Manufacturer Specification Sheet Test Conditions				
Manufacturer	**Product**	**Permeate Flow (m^3/d)***	**Area (m^2)***	**Feed Concentration (mg/L NaCl)**	**Pressure (psi)**	**Stabilized Salt Rejection (%)**
Dow Filmtec	**NF 270 –** Nanofiltration	47	37	2,000 $MgSO_4$	70	97
GE	**AP Series-** Extreme Low Pressure Brackish Water RO	47.2	37.1	500	75	95.0
Hydranautics	**ESPA2-LD** Energy Saving Polyamide membrane	37.9	37.1	1,500	150	99.6
Toray	**TMG(D)-**Ultra Low Pressure Brackish Water RO	45.8	37	2,000	150	99.7
Dow Filmtec	**BW30XFRLE-** Brackish Water RO	43	37	2,000	150	99.3
GE	**AG LF Series-** Standard Brackish Water RO	39.7	37.2	2,000	225	99.5
Dow Filmtec	**SW30XHR-** High Rejection Seawater RO	23	37	32,000	800	99.82
Toray	**TM800M-**Standard Seawater RO	26.5	37	32,000	800	99.8

*Permeate flow and area are for 8 inch diameter and 40 inch long membrane elements.

Table 2.2: Membranes chosen for experiments with tested pressures

Manufacturer and Product	Type of Membrane*	Test Group Number	Pressures Used in Test (psi)		
			High Pressure	Medium Pressure	Low Pressure
GE AF-LF	BW	2	225	150	75
Dow Filmtec BW30XFRLE					
Hydranautics ESPA2-LD					
Toray TMG(D)					
Dow Filmtec SW30XHR	SW	3	350	225	150
Toray TM800M					
GE AP	ULP	1	100	75	50
Dow Filmtec NF 270					

*SW=sea water, BW=brackish water, ULP=ultra-low pressure

2.3 Feed water Composition

During the first phase of experiments, the feed water consisted of deionized water. The purpose of this phase was to compact the membrane material, as well as to clean the membrane products of any preservative. This water was changed to fresh deionized water at 2,4, and 6 hours during the total 24 hours of this phase. Both Phase 2 and 3 feed solutions were kept at a constant pH of 6.5 by adding 1.6 mM sodium phosphate and 0.4 mM disodium phosphate. The pH of 6.5 was chosen based on the pH generally used in reuse practices. The feed solution in Phase 2 also consisted of the buffered deionized water with 2,000 mg/L NaCl and 5 mg/L H_3BO_3.

In Phase 3, the feed solution contained the target organic compounds in the buffered deionized water. The target organic compounds consisted of up to 73 compounds that represent the various organic chemistry groups. Table 2.3 shows a complete list of the 73 organic compounds that were used in this study, along with the molecular weight and log K_{ow} of each compound.

The list contains alcohols, aromatics, esters, ethers, haloalkanes, haloalkenes, nitriles, and ketones. The molecular weights of the compounds range from 41 to 260 g/mol and log K_{ow} values range from -0.34 to 4.78. Large variations of organic compounds were chosen in order to have a wide range of organic mass transfer coefficients to compare to the boron mass transfer coefficient. Furthermore, the tested compounds contained a variety of different functional groups for comparison of effects of functional groups on organic compounds rejection by RO membranes.

Table 2.3: Organic compounds tested in experiments

Compound	Compound Category	MW (g/mol)	log K_{OW}
1,1-Dichloroethane	Haloalkane	98.96	1.79
1,1-Dichloroethene	Haloalkene	98.96	1.79
1,1-Dichloropropene	Haloalkene	110.97	N/A
1,1,1-Trichloroethane	Haloalkane	133.40	2.49
1,1,1,2-Tetrachloroethane	Haloalkane	167.85	2.93
1,1,2-Trichloroethane	Haloalkane	133.40	1.89
1,1,2,2-Tetrachloroethane	Haloalkane	167.85	2.39
1,2-Dibromo-3-chloropropane	Haloalkane	236.33	2.96
1,2-Dibromoethane (EDB)	Haloalkane	187.86	1.96
1,2-Dichlorobenzene	Aromatic	147.00	3.43
1,2-Dichloroethane (EDC)	Haloalkane	98.96	1.48
1,2-Dichloropropane	Haloalkane	112.99	1.98
1,2,3-Trichlorobenzene	Aromatic	181.45	4.05
1,2,3-Trichloropropane	Haloalkane	147.43	2.27
1,2,4-Trichlorobenzene	Aromatic	181.45	4.02
1,2,4-Trimethylbenzene	Aromatic	120.19	3.78
1,3-Dichlorobenzene	Aromatic	147.00	3.53
1,3-Dichloropropane	Haloalkane	112.99	2.00
1,3,5-Trimethylbenzene	Aromatic	120.19	3.42
1,4-Dichlorobenzene	Aromatic	147.00	3.44
1,4-Dioxane	Ester	88.11	-0.27
2-Butanone	Ketone	72.11	0.29
2-Chlorotoluene	Aromatic	126.58	3.42
2-Hexanone	Ketone	100.16	1.38
2,2-Dichloropropane	Haloalkane	112.99	1.98
4-Chlorotoluene	Aromatic	126.58	3.33
4-Isopropyltoluene	Aromatic	134.22	4.10
Acetone	Ketone	58.08	-0.24
Acetonitrile	Nitrile	41.05	-0.34
Acrylonitrile	Nitrile	53.06	0.25
Benzene	Aromatic	78.11	2.17
Bromobenzene	Aromatic	157.01	2.99
Bromochloromethane	Haloalkane	129.38	1.41
Bromodichloromethane	Haloalkane	163.83	2.00
Bromoform	Haloalkane	252.73	2.40
Bromomethane	Haloalkane	94.94	1.19
Carbon Tetrachloride	Haloalkane	153.82	2.83
Chlorobenzene	Aromatic	112.56	2.84
Chloroethane	Haloalkane	64.51	1.43

Chloroform	Haloalkane	119.38	1.97
Chloromethane	Haloalkane	50.49	0.91
cis-1,2-DCE	Haloalkene	96.94	1.86
cis-1,3-Dichloropropene	Haloalkene	110.97	2.06
Dibromochloromethane	Haloalkane	208.28	2.16
Dibromomethane	Haloalkane	173.84	1.70
Dichlorodifluoromethane	Haloalkane	120.91	2.16
Ethylbenzene	Aromatic	106.17	3.15
Hexachlorobutadiene	Haloalkene	260.76	4.78
Isopropyl alcohol	Alcohol	60.10	0.05
Isopropyl ether	Ether	102.17	N/A
Isopropylbenzene	Aromatic	120.19	3.66
m-xylenes	Aromatic	106.17	3.15
Methyl tert-butyl ether (MTBE)	Ether	88.15	0.94
Methylene Chloride	Haloalkane	84.93	1.25
MIBK	Ketone	100.16	1.31
n-Butylbenzene	Aromatic	134.22	4.38
n-Propylbenzene	Aromatic	120.19	3.69
Naphthalene	Aromatic	128.17	3.30
o-Xylene	Aromatic	106.17	3.12
p-Xylenes	Aromatic	106.17	3.15
sec-Butylbenzene	Aromatic	134.22	4.57
Styrene	Aromatic	104.15	2.95
tert-Amyl methyl ether	Ether	102.17	1.55
tert-Butyl alcohol	Alcohol	74.12	0.35
tert-Butyl ethyl ether	Ether	102.18	1.92
tert-Butylbenzene	Aromatic	134.22	4.11
Tetrachloroethene (PCE)	Haloalkene	165.83	3.40
Toluene	Aromatic	92.14	2.73
trans-1,2-DCE	Haloalkene	96.94	2.06
trans-1,3-Dichloropropene	Haloalkene	110.97	1.82
trans-1,4-Dichloro-2-butene	Haloalkene	125.00	N/A
Trichloroethene (TCE)	Haloalkene	131.39	2.61
Vinyl acetate	Ester	86.09	0.73
Vinyl chloride	Haloalkene	62.50	1.62

2.4 Experimental Procedures

Each of the three experiments, one for each membrane group, was conducted in three separate phases described in detail in Table 2.4 to 2.7. The cross flow velocity was chosen based on general RO practice in wastewater reclamation processes. The experimental plans for each group of membranes are provided in greater detail in Appendix B to D.

Table 2.4: Test parameters held constant for all 3 phases of experiments

Experimental Parameters Held Constant for All 3 Phases	
Feed Tank Volume (L)	20
Feed Temperature (°F)	68
Cross Flow Velocity (m/s)	0.25
pH (Phase 2 and 3 only)	6.5

Table 2.5: Test parameters for Phase 1

Phase 1: DI Water Cleaning and Compaction	
Feed Pressure (bar)	High pressure for membrane group
Duration (hours)	24
Sample Procedure	No sampling

Table 2.6: Test parameters for Phase 2

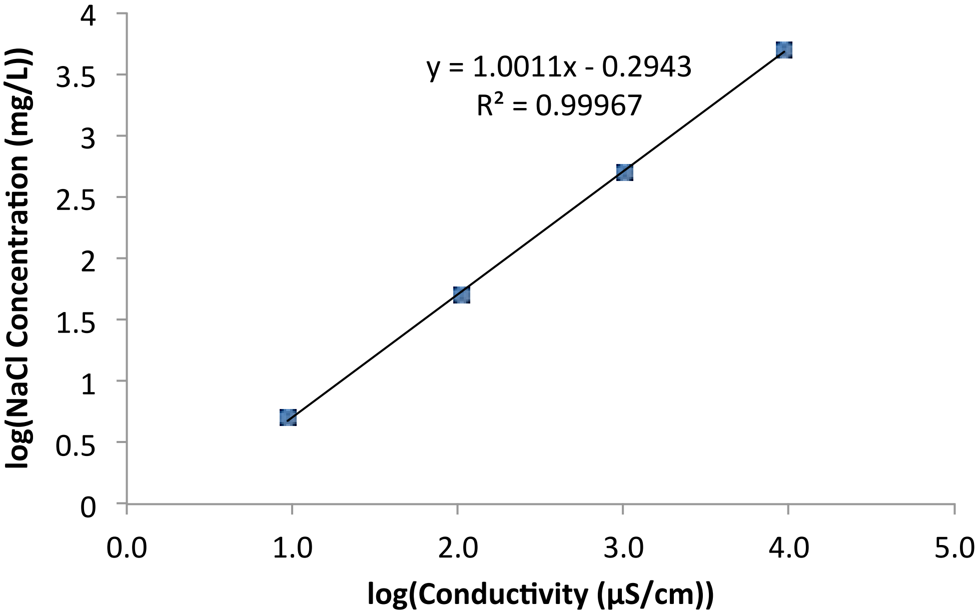
Phase 2: NaCl and Boron Rejection Test Parameters	
Feed Pressure (bar)	Medium pressure for membrane group
Duration (hours)	24
Concentration (mg/L)	NaCl: 2,000 Boron: 5
Measurements taken per sample	Conductivity, pH, boron
Sample Procedure	• Initial feed tank sample • Each permeate, feed, and concentrate after 24 hours of testing

Table 2.7: Test parameters for Phase 3

Phase 3: Organics Rejection Test Parameters	
Feed Pressure (bar)	Run at the high pressure for the membrane group for 72 hours, then medium and low pressures for the membrane group for sampling at end of test
Duration (hours)	72
Concentration (µg/L)	Dependent on compound, see Table 2.3
Sample Procedure	• Initial feed tank sample • Each permeate, feed tank, and concentrate after 72 hours of testing • Reduce to medium pressure, wait one hour, sample each permeate, feed tank • Reduce to low pressure, wait one hour, sample each permeate, feed tank

2.5 Analytical Methods

An Oakton PC 2700 conductivity meter was used to measure electrical conductivity. A calibration curve relating NaCl concentration and conductivity was developed to calculate the NaCl concentration in solution. Figure 2.4 shows this calibration curve.



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The concentration of boron in solution was analyzed using a PerkinElmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) with a detection limit of < 0.01 mg/L.

Hall Environmental, a commercial EPA certified lab in Albuquerque, New Mexico completed the organic compound analysis. Hall Environmental used EPA Method 5030 (Purge and Trap) for extraction and quantified the compounds using EPA Method 8260 (Volatile Organic Compound Analysis by GC/MS) (Techniquea, 1996). This method is used to determine concentrations of volatile organic compounds. It can be used to measure most volatile organic compounds that have boiling points below 200 °C.

2.6 Data Analysis

The analysis used in this study is based on the solution diffusion model of permeation through RO membranes. The solution diffusion model is used to describe mass transfer through reverse osmosis membranes. In this study, the following equations describing the solution diffusion model were used (Howe et al., 2012, Wijmans et al., 1995).

Rejection refers to the inability of a constituent to pass through the RO membrane, and is usually reported in percent (%). Equation 2.1 is used to calculate rejection (Howe et al., 2012).

$Rej = 1 - \frac{C_P}{C_F}$ **Equation 2.1**

where:

$Rej = rejection\ (dimensionless)$

$C_P = concentration\ in\ the\ permeate\ \left(\frac{mg}{L}\right)$

$C_F = concentration\ in\ the\ feed\ \left(\frac{mg}{L}\right)$

A minimum rejection value was calculated when the values of rejection were calculated as negative or the permeate values were non-detect. The negative calculated rejections were corrected to zero based on an assumption that negative rejections are physicall not possible. For non-detect permeate values, the detection limit was as assumed to be the permeate concentration value in the rejection calculation. If the feed concentration was reported as non-detect in the sample, the rejection was reported as "NA".

In this study, water flux was calculated based on a measured flow through each membrane and the known membrane area, which is described in Equation 2.2. The water flux was then used to calculate the mass transfer coefficient for water, or the k_w, presented in Equation 2.3. The determination of β is described below.

$J_W = \frac{Q}{A}$ **Equation 2.2**

where:

$\mathrm{J_W} = \text{volumetric flux of water}\ \left(\frac{\mathrm{L}}{\mathrm{m^2 \cdot h}}\right)$

$\mathrm{Q} = \text{measured water flow}\left(\frac{\mathrm{L}}{\mathrm{h}}\right)$

$\mathrm{A} = \text{membrane area}\ (m^2)$

$J_W = k_W(\Delta P - \Delta\pi)$ **Equation 2.3**

where:

$\mathrm{k_W}$ = mass transfer coefficient for water $\left(\frac{\mathrm{L}}{\mathrm{m^2 \cdot h \cdot bar}}\right)$

ΔP = pressure difference across the membrane (bar)

$\Delta\pi = \beta\pi_{Feed} - \pi_{Permeate}$

= osmotic pressure differential across the membrane (bar)

β = concentration polarization factor (dimensionless)

The solute mass transfer coefficient, k_s is described in Equation 2.4 below. The solute flux, J_s, through RO membranes is driven by the difference in concentration on each side of the membrane. The concentration of the solute in the permeate is described as a ratio of the solute flux and water flux, as presented in Equation 2.5. The higher the flux of water, the lower the rejection of solutes through the RO membrane is.

$J_s = k_s \Delta C$ **Equation 2.4**

where:

$\mathrm{J_s}$ = mass flux of solute $\left(\frac{\mathrm{mg}}{\mathrm{m^2 \cdot h}}\right)$

$\mathrm{k_S}$ = mass transfer coefficent for solute flux $\left(\frac{\mathrm{L}}{\mathrm{m^2 \cdot h}}\right)$

$\Delta \mathrm{C} = \beta \mathrm{C_{Feed}} - \mathrm{C_{Permeate}}$ = difference in concentration across membrane (mg)

$C_{Permeate} = \frac{J_S}{J_W}$ **Equation 2.5**

The $\mathrm{k_W}$ was calculated from the operating parameters (i.e. water flux and pressures) and β mentioned above for each phase of the experiments at the three different phases. The average was then taken of the $\mathrm{k_W}$ values from all phases of the experiment, including the three calculated $\mathrm{k_W}$ values from each pressure of the organics portion of the experiment. This average $\mathrm{k_W}$ value for each membrane was used in Equation 2.6 below to calculate the solute mass transfer coefficient, or the k_s. When the rejection values were zero for any given compound, the k_s could not be determined.

$k_S = \left(\frac{1-Rej}{Rej}\right)\left(\frac{k_W(\Delta P - \Delta\Pi)}{\beta_0}\right)$ **Equation 2.6**

where:

$\beta_0 = e^{Jw/k_{CP}}\ (dimensionless)$

Concentration polarization was taken into account for all experiments. Concentration polarization happens when the concentration of constituents in the bulk fluid is less than their concentration at the membrane surface, causing an increased concentration gradient at the surface of the membrane. As solutes in the water flow towards the membrane surface, clean water will pass through the membrane. This creates a boundary layer at the feed-concentrate side of the membrane. Equation 2.7 describes the relationship between the concentration of the membrane and bulk fluid flow, where the concentration at the membrane surface is equal to the bulk fluid concentration multiplied by the concentration polarization factor.

Taking a mass balance of the boundary layer at the membrane surface, combined with Equation 2.7 and Equation 2.1 results in Equation 2.8 below, which describes the extent of the concentration polarization. Equation 2.8 can be simplified to Equation 2.9 when rejection is greater than 99%.

$$\beta = \frac{C_M}{C_B} \qquad \textbf{Equation 2.7}$$

where:

$\beta =$ the concentration polarization factor (dimensionless)

$C_M =$ concentration of solutes at membrane surface (mg/L)

$C_B =$ concentration of solutes in the bulk fluid (mg/L)

$$\beta = (1 - Rej) + Rej\left(e^{Jw/k_{CP}}\right) \qquad \textbf{Equation 2.8}$$

$$\beta = e^{Jw/k_{CP}} = \beta_0 \qquad \textbf{Equation 2.9}$$

where:

$k_{CP} = \lambda \frac{D_L}{d_H}(Re)^{0.50}(Sc)^{1/3} =$ concentration polarization mass transfer coefficient $\left(\frac{m}{s}\right)$

λ (dimensionless) = empirical parameter

$\mathrm{d_H}$ = hydraulic diameter (L)

$\mathrm{Re} = \frac{\rho v d_H}{\mu}$ = Reynolds number (dimensionless)

$\mathrm{Sc} = \frac{\mu}{\rho D_L}$ = Schmidt number (dimensionless)

v = velocity in feed channel $\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$

ρ = feed water density $\left(\frac{\mathrm{kg}}{m^3}\right)$

μ = feed water dynamic viscosity $\left(\frac{\mathrm{kg}}{\mathrm{m} \cdot \mathrm{s}}\right)$

$\mathrm{D_L}$ = diffusion coefficient for solute in water $\left(\frac{\mathrm{m}^2}{\mathrm{s}}\right)$

The values used for the λ, hydraulic diameter, Reynolds and Schmidt number, and membrane area are presented in Table 2.8. The diffusion coefficient for the organics portion of the test is presented in Table 2.8. This value was used as the diffusion coefficient because it was found to be approximately the average of all the organics diffusion coefficients. Also, it was found that changing this value did not have much of an impact on the concentration polarization value. Therefore, it was found to be reasonable to assume that this average value for the diffusion coefficient could be used. The diffusion coefficient for the phosphate buffer was calculated using the Nernst-Haskell equation (Poling et al., 2001).

Table 2.8: Parameters used in equations

Parameter	Value
λ	0.47
d_H (m)	0.00146
Re (unitless)	161.3
Sc (unitless)	1592.1
D_L $(\frac{m^2}{s})$ (for sodium chloride)	1.58×10^{-9}
D_L $(\frac{m^2}{s})$ (for organics)	1.12×10^{-9}
Membrane Area (m^2)	0.016

3. Comparison of Rejection for Organic Compounds

3.1 Organic Compounds and Properties

The organic compounds were chosen to provide a wide range of functional groups. Few studies have chosen organic compounds specifically to look at the effects of different functional groups on rejection through RO membranes. Instead, previous studies chose organics based on relevance to industry or to provide a variety of the molecular property being investigated. The organics tested are broken into 5 different categories for comparison; halobenzenes, alkylbenzenes, haloalkenes, haloalkanes, and oxygenated compounds. Within these 5 groups, 6 sets of structural isomers are compared. From gaining perspective at the structural level of each organic and how it is rejected, the general rules thought to guide rejection of organics through RO membranes can be examined closely. The objective of this study was to compare the rejection of organics with different functional groups. This will be done to gain insight into what changes in functional groups and molecular structure affect rejection from a fundamental point of view.

The two organic properties chosen for investigation in this study are molecular weight and log K_{ow}. These two properties describe two main rejection mechanisms of organic compounds; size exclusion and chemical interactions with the membrane surface. The molecular weight of organics is roughly correlated to the size of each molecule affects rejection by RO membranes. Log K_{ow} is a parameter that is indicative of the compound's general behavior in aqueous solution, which will also affect membrane performance. This section discusses the importance of functional groups on rejection of organic compounds. All of the chemical properties listed in Tables 3.1 to 3.5 were found on the SRC PhysProp database.

3.2 Data Analysis

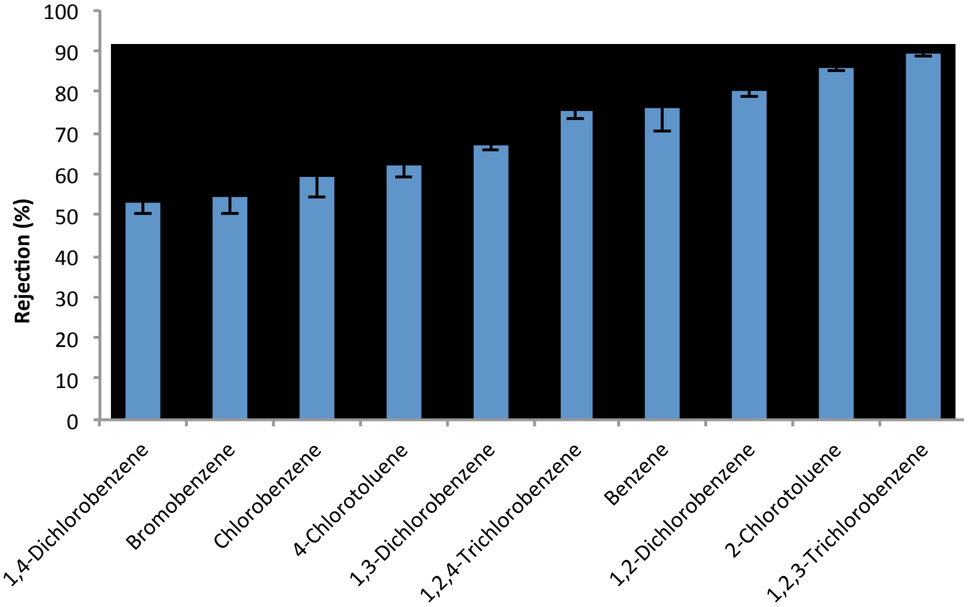
For the discussion this section, only the Hydranautics ESPA2-LD membrane was chosen for analysis. This brackish water membrane was chosen because of its widespread use in water reuse facilities.

Analysis of the organic compounds was completed by first analyzing each organic's k_s value through the Hydranautics ESPA2-LD membrane. This membrane was tested in the first and last cell in the system, providing duplicate measurements for all k_s values at each test pressure. At the lowest test pressure for each membrane group, the last membrane in the series was sampled in triplicate measurements.

This resulted in 8 calculated k_s values to compare to each other. Although the k_s values were determined at different operating pressures, the solution/diffusion model suggests that the k_s value should be constant for each organic through each membrane; therefore, the k_s values can be treated as replicates. The k_s values were compared to each other by taking the relative standard deviation (RSD) of the k_s measurements for each organic. If the RSD was calculated to be 0.5 or greater, that compound was considered to have poor repeatability and thus was no longer considered for further analysis. Furthermore, if the permeate concentration was reported as not detected, the detection limit was used to calculate the rejection. This resulted in some rejection values shown in this section to represent the lowest measureable rejection instead of the actual rejection. Of the 72 total organic compounds tested, 54 compounds had data that met the criteria for analysis. The 5 groups of compounds were the focus for the remaining analysis of the ESPA2-LD membrane. The error bars on each graph below represents the standard deviation between each of the 8 experimental rejection values for the ESPA2-LD membrane.

3.3 Halobenzenes

Figure 3.1 shows rejection data for the halobenzenes through the ESPA2-LD membrane. Rejection does not correlate to either molecular weight or log K_{ow} (Figure 3.2). The properties of these compounds can be seen in Table 3.1.



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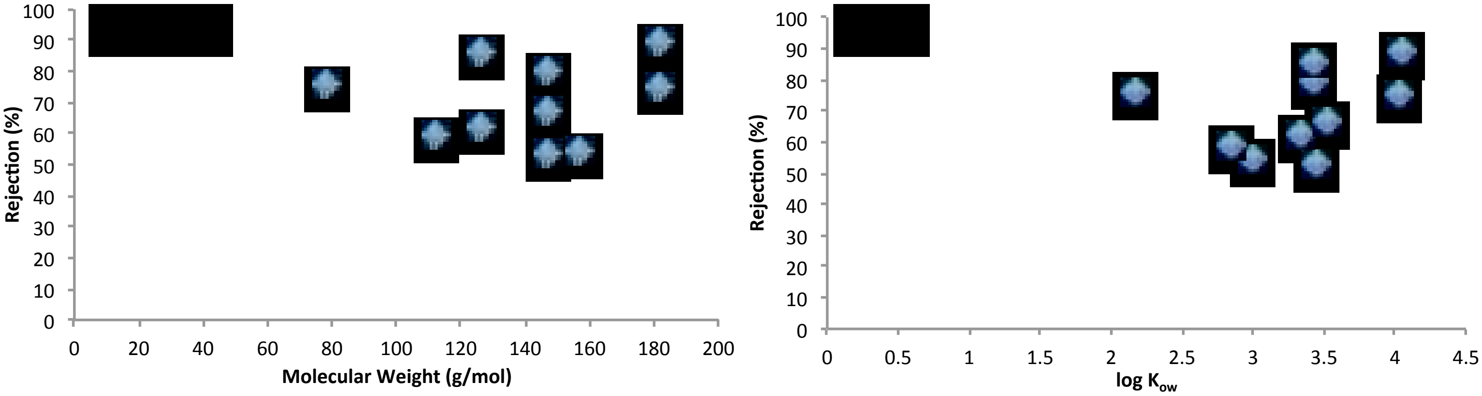

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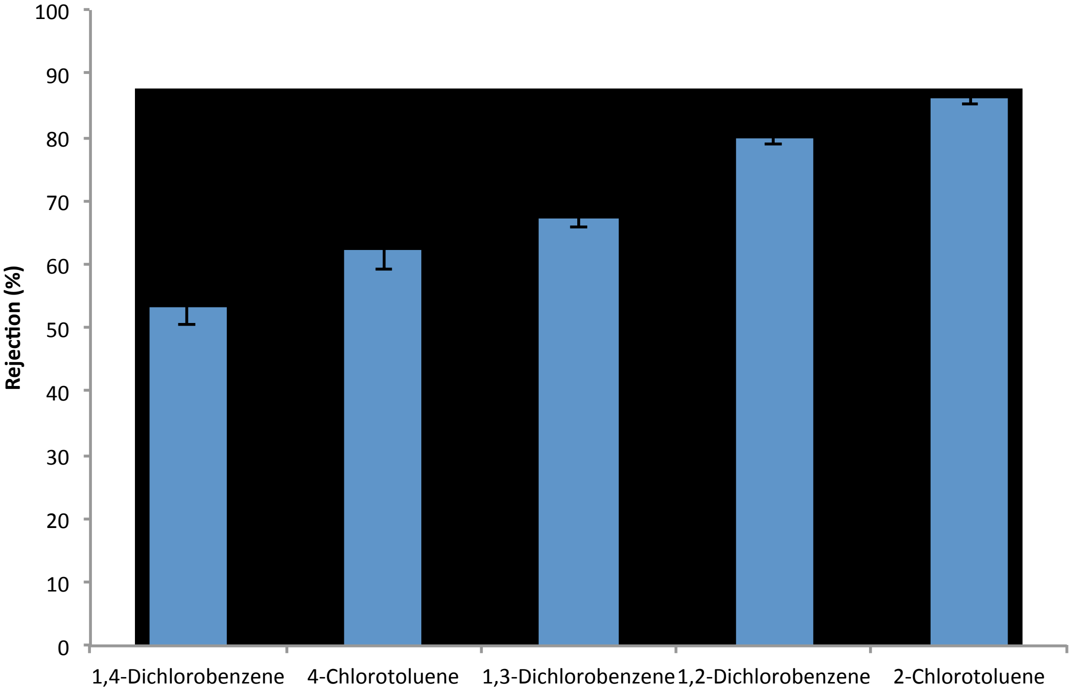
Table 3.1: Molecular weight and log K_{ow} of the halobenzenes

Compounds	Molecular Weight (g/mol)	log K_{ow}
1,4-Dichlorobenzene	147.00	3.44
Bromobenzene	157.01	2.99
Chlorobenzene	112.56	2.84
4-Chlorotoluene	126.58	3.33
1,3-Dichlorobenzene	147.00	3.53
1,2,4-Trichlorobenzene	181.45	4.02
Benzene	78.11	2.13
1,2-Dichlorobenzene	147.00	3.43
2-Chlorotoluene	126.58	3.42
1,2,3-Trichlorobenzene	181.45	4.05

The two compounds containing one functional group are chlorobenzene and bromobenzene. It was expected that because bromobenzene has a higher molecular weight and higher log K_{ow} than chlorobenzene, that it would have a higher rejection than chlorobenzene. Bromobenzene had a lower rejection than chlorobenzene, though, by about 5%. This difference in rejection could be due to experimental error, however. Both chlorobenzene and bromobenzene had a lower rejection than benzene. Because benzene does not contain any functional groups, it has the lowest molecular weight of all the aromatics tested. Benzene has a lower log K_{ow} than both chlorobenzene and bromobenzene, which would give benzene an expected rejection below most of the halobenzenes. The rejection of benzene is 15% greater than chlorobenzene, however. This suggests that the interaction of the halogen atom with the membrane is important in these organics rejection through RO membranes.

The two halobenzenes with three halogens are the two isomers 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene, which is presented in Figure 3.1. Structural hindrance of each molecule could be a possible explanation of the difference in rejection between these two compounds, as they have identical molecular weights and log K_{ow} values. The chlorine in the 4th position being farther away from the other two in 1,2,4-trichlorobenzene causes the molecule to be less structurally hindered than 1,2,3-trichlorobenzene. This suggests that 1,2,4-trichlorobenzene has a greater chance to interact with the membrane material, resulting in the 15% lower rejection of 1,2,4-trichlorobenzene when compared to 1,2,3-trichlorobenzene.



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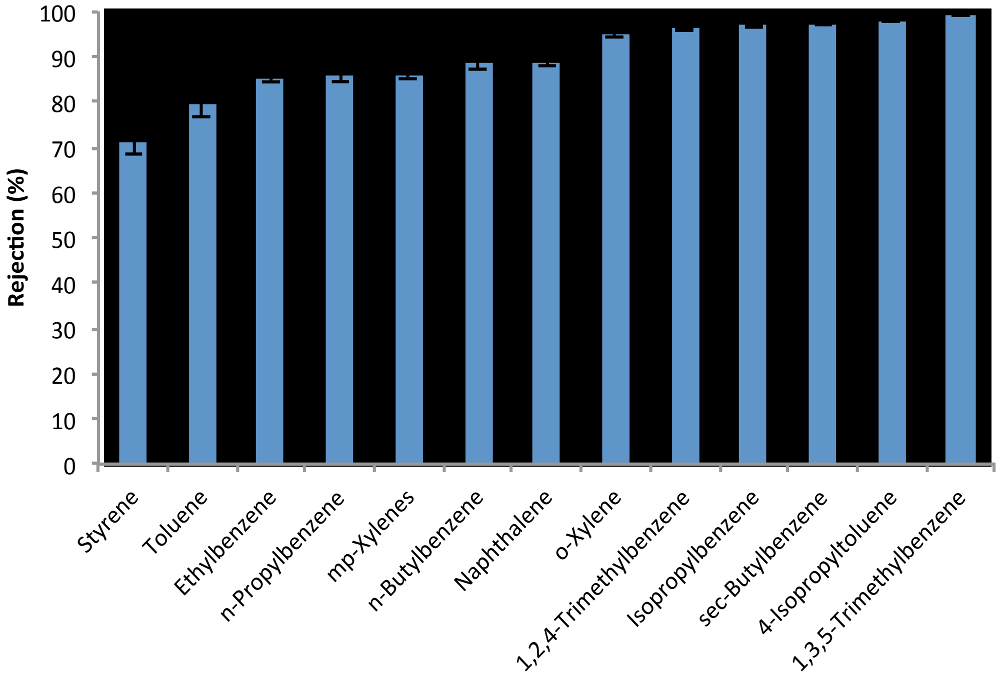
The halobenzenes with two functional groups are presented in Figure 3.3. This figure suggests structural hindrance of the organic molecule is important when considering mass transfer of organics through RO membranes. Two sets of structural isomers exist in this group; the two chlorotoluenes and the three dichlorobenzenes. The compound with the lowest rejection of all halobenzenes is 1,4-dichlorobenzene, which has two chlorine functional groups on either side of the benzene ring. The most structurally hindered compound of the dichlorobenzenes is 1,2-dichlorobenzene, which has the highest rejection of the three structural isomers. The structural hindrance of the molecule itself seems to be important when considering the difference of rejection between these structural isomers. The difference in rejection between 4-chlorotoluene and 2-chlorotoluene could also be contributed to a difference in structural hindrance of the molecule itself.

Comparing the dichlorobenzenes to the two cholortoluene suggests the importance of structural hindrance of a molecule on organic compound rejection. These compounds have very similar log K_{ow} values. The three dichlorobenzenes weigh more than the two chlorotoluene isomers, which do not follow the expected trends. The methyl group in 4-chlorotoluene is "bulkier" than the chlorine in 1,4-dichlorobenzene resulting in a higher rejection than by about 10%. The same trend can be seen between 1,2-dichlorobenzene and 2-chlorotoluene, where the difference in their rejections is about 6%.

3.4 Alkylbenzenes

Figure 3.4 shows rejections of all alkylbenzenes tested by the ESPA2-LD membrane. The alkylbenzenes all had high rejections, with half of the 12 alkylbenzenes tested having rejections over 90%. Styrene is the lowest rejected



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compound of this group at 70%. Figure 3.5 presents the trends between rejection and molecular weight and log K_{ow}. This figure shows there is no linear relationship between these properties and the rejection of the compounds. The properties of the alkylbenzenes can be seen in Table 3.2.

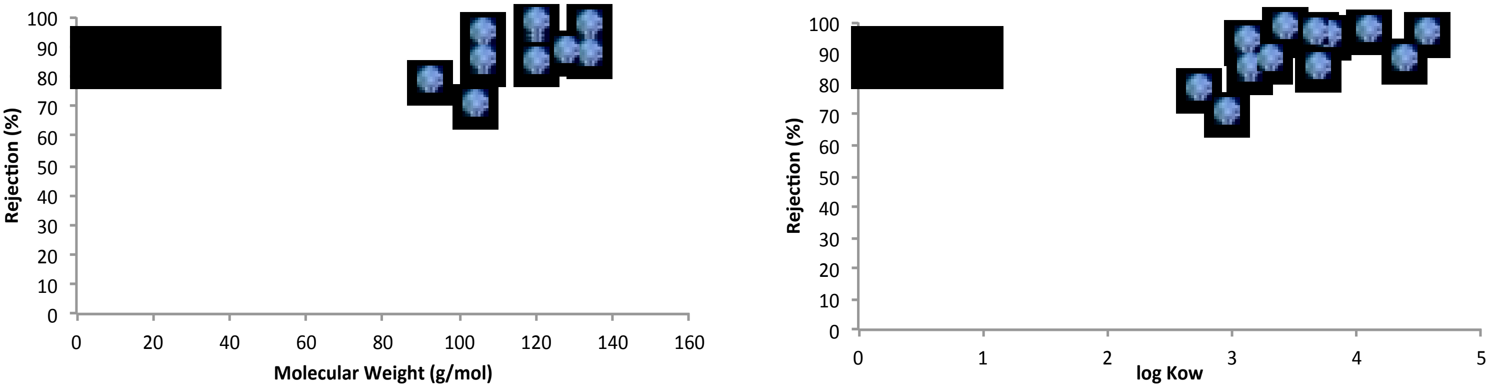

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Table 3.2: Molecular weight and log Kow of the alkylbenzenes

Compounds	Molecular Weight (g/mol)	log K_{ow}
Styrene	104.15	2.95
Toluene	92.14	2.73
Ethylbenzene	106.17	3.15
n-Propylbenzene	120.19	3.69
m-xylenes	106.17	3.20
p-xylene	106.17	3.15
n-Butylbenzene	134.22	4.38
Naphthalene	128.17	3.30
o-Xylene	106.17	3.12
1,2,4-Trimethylbenzene	120.19	3.63
Isopropylbenzene	120.19	3.66
sec-Butylbenzene	134.22	4.57
4-Isopropyltoluene	134.22	4.10
1,3,5-Trimethylbenzene	120.19	3.42

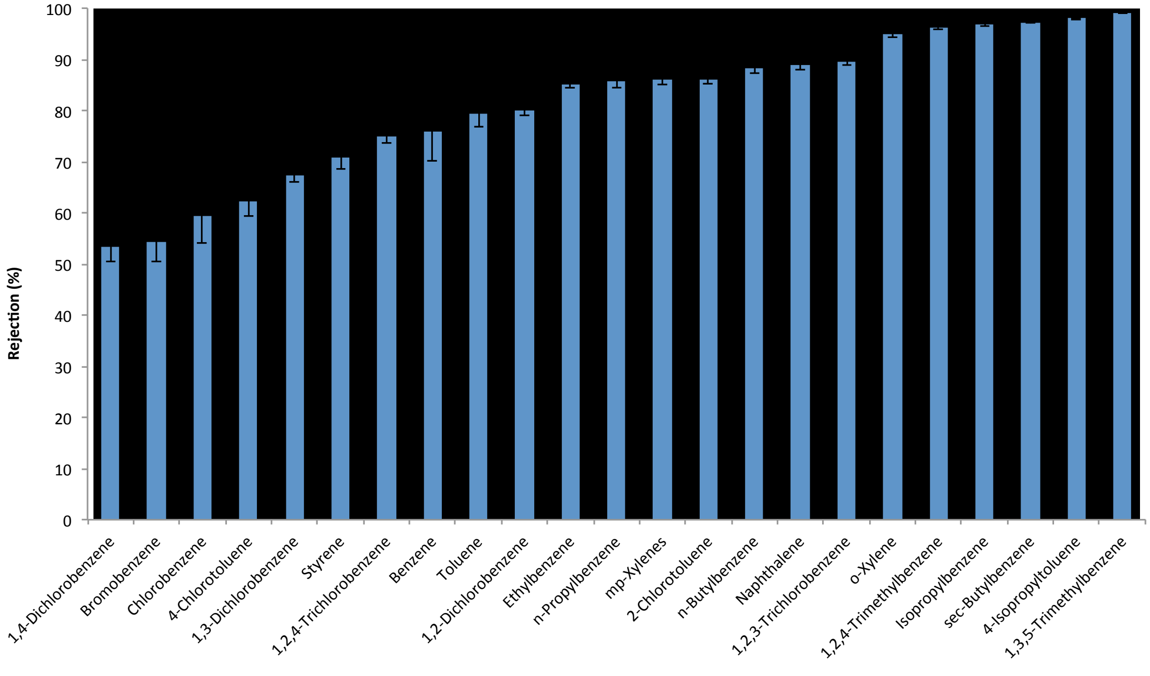
The alkylbenzene compounds containing one function group are styrene, toluene, ethylbenzene, n-propylbenzene, n-butylbenzene, naphthalene, isopropylbenzene, and sec-butylbenzene. As the number of carbons on the functional group increases, the rejection of these alkylbenzenes generally increases as well. Toluene contains a methyl group and is rejected 6% lower than ethylbenzene and n-propylbenzene, which contain an ethyl and propyl functional groups. N-butylbenzene is rejected slightly higher than ethylbenzene and n-propylbenzene, and also has a very similar rejection with naphthalene. Furthermore, when comparing these compounds that contain the same number of carbon atoms in the alkyl functional group, more branched alkyl groups leads to a higher rejection. This trend can be seen between n-propylbenzene and isopropylbenzene, which both contain three carbon atoms in their functional group. The difference in rejection between these compounds is about 11%. The same trend can be seen between n-butylbenzene and sec-butylbenzene. N-butylbenzene contains the functional group with less branching when compared to sec-butylbenzene, and showed about 9% less rejection.

The three alkylbenzenes containing two functional groups are the two xylene isomers and 4-isopropyltoluene. The two xylene isomers have similar molecular properties, however, o-xylene has about a 10% higher rejection. O-xylene contains methyl functional groups on the 1st and 2nd carbons on the benzene ring. M-xylene and p-xylene have methyl groups on the 1st carbon, and either the 3rd or 4th carbon. The methyl groups being closer together on o-xylene could lead to a lower interaction with the membrane material, resulting in the higher rejection. 4-isopropyltoluene has a rejection 12% higher than m-xylene and p-xylene, which is to be expected. These two compounds are similar, with the difference between the two being an isopropyl group in place of a methyl on the 4th carbon. Since 4-isopropyltoluene has a higher molecular weight and log K_{ow}, it is expected that it have a large rejection.

Both isomers of 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene have similar rejections, with only a 3% difference. These two compounds having very high rejections, 96% and 99%, are expected, as both compounds are very large and have high log K_{ow} values. Although it is difficult to discuss trends between these two compounds considering their relatively high and similar rejections, it is interesting that 1,2,4-trimethylbenzene is rejected slightly lower than 1,3,5-trimethylbenzene. The previous hypothesis that the more spread out the functional groups are on the compounds, the lower the rejection may not be true for these compounds. This is the only isomer group that does not follow this hypothesis. Furthermore, 1,3,5-trimethylbenzene also has a lower log K_{ow} value than 1,2,4-trimethylbenzene, which should result in a higher rejection. A parameter or molecular property describing the interaction of these two molecules with the membrane material should be investigated further to gain a better understanding of the differences in rejection between these molecules. However, since the difference in their rejection is very small, this observed trend could be due to analytical error in the concentration measurements.

3.5 Halobenzenes and Alkylbenzenes

Although the halobenzenes generally have a higher molecular weight than the alkylbenzenes, the alkylbenzenes show higher rejection than the halobenzenes. Figure 3.6 presents all halobenzenes and alkylbenzenes rejection by the ESPA2-LD membrane.



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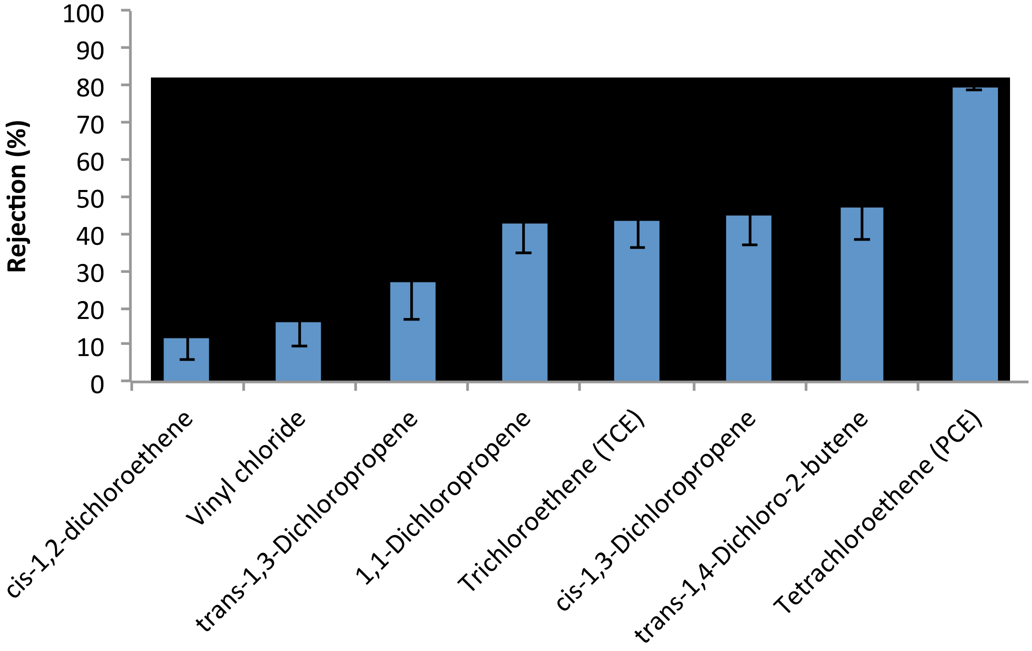
These results could suggest a couple of possibilities. The interactions between the halogens with the membrane could provide less rejection for these organic compounds. The halogen functional groups could possibly be interacting with the membrane material, allowing these compounds to pass through the membrane. Also, the alkylbenzenes having higher rejection could be due to the alkyl groups being larger than halogens. Although halogens weigh more than methyl groups, a methyl group contains one carbon and three hydrogen atoms and therefore takes up more space around the molecule. This could cause the alkylbenzenes to be rejected based on size exclusion, or the compounds not being able to fit to interact with the membrane material. These results suggest that only using molecular weight to describe size exclusion of molecules through RO membranes may not present a complete understanding of the rejection mechanism of size exclusion.

3.6 Haloalkenes

Presented in Figure 3.7 are all 10 of the haloalkenes tested. The haloalkene used in this study were limited to chlorinated compounds. Generally, all haloalkenes showed poor rejection, with 7 out of the 8 compounds having less than 50% rejection. The highest rejected haloalkene was tetrachloroethene (PCE) at 80% rejection. The rejection of the haloalkene compounds do correlate linearly to molecular weight and log K_{ow}. Figure 3.8 shows these relatively linear relationships, suggesting that both molecular weight and log K_{ow} may be important when considering haloalkene rejection. Table 3.3 contains the haloalkenes molecular properties.



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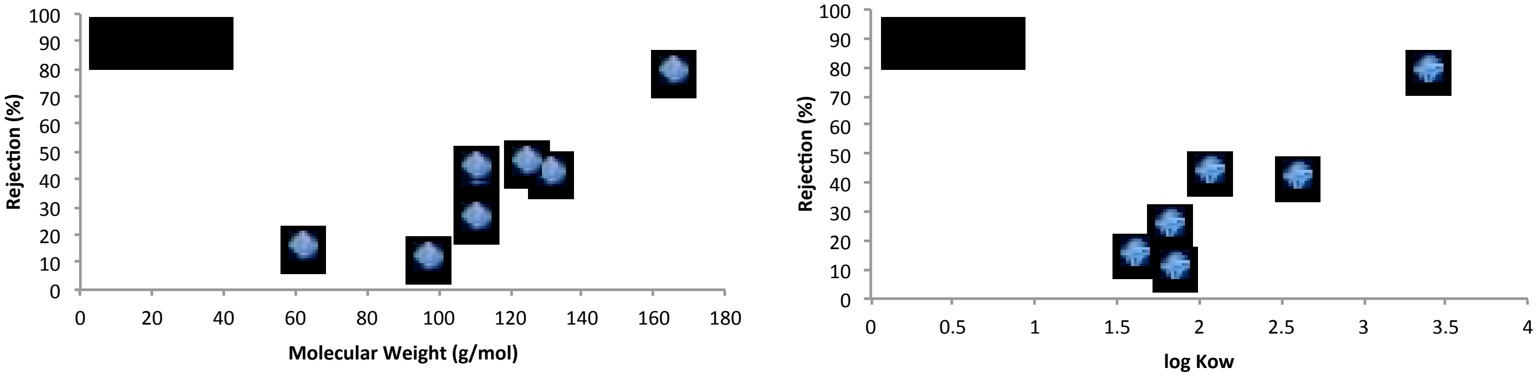

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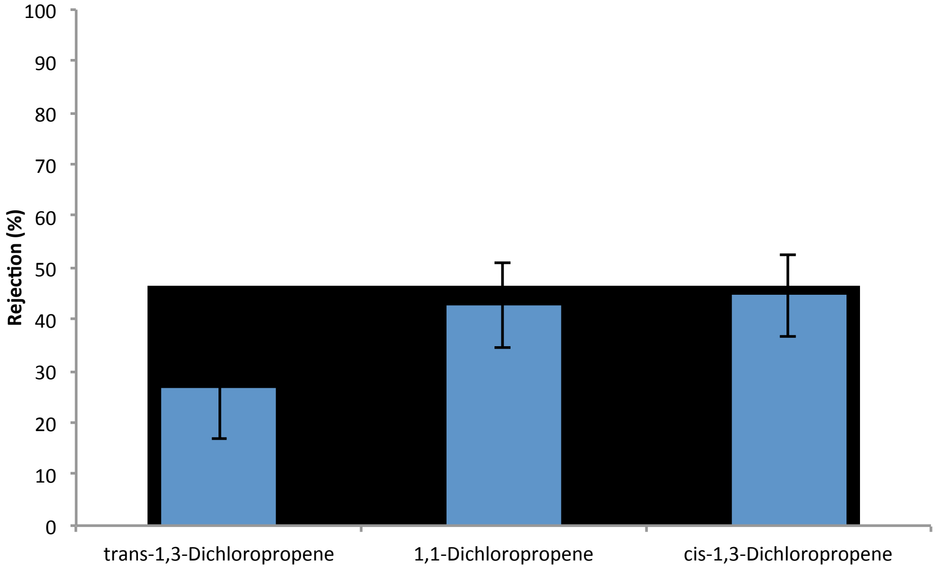
Table 3.3: Molecular weight and log K_{ow} of the haloalkenes

Compounds	Molecular Weight (g/mol)	log K_{ow}
cis-1,2-Dichloroethene (DCE)	96.94	2.00
Vinyl chloride	62.50	1.62
trans-1,3-Dichloropropene	110.97	2.03
1,1-Dichloropropene	110.97	2.53
Trichloroethene (TCE)	131.39	2.42
cis-1,3-Dichloropropene	110.97	2.06
trans-1,4-Dichloro-2-butene	125.00	2.60
Tetrachloroethene (PCE)	165.83	3.40

Vinyl chloride is the only compound out of the haloalkenes containing one chlorine atom as a functional group. Vinyl chloride and cis-1,2-dichloroethene (cis-1,2-DCE) have only a 4% difference in rejection. However, this difference may not be relevant due to the analytical variability in the measurement of these compounds. The structural difference between these molecules is two chlorine atoms on the same side of cis-1,2-DCE, and only one chlorine atom connected to the carbon double bond in vinyl chloride. Although cis-1,2-DCE has a higher molecular weight and log K_{ow}, its slightly lower rejection could be due to an interaction of the chlorine atoms with the membrane material.

The difference in rejection between TCE and PCE is 36%. The difference between these two molecules is one added chlorine functional group in PCE. The addition of this chlorine as a functional group gives PCE a higher molecular weight and log K_{ow}, which could all lead to the increase in rejection. As discussed earlier, PCE is the highest rejected haloalkene at 80%. The next highest rejected compound at 47% is trans-1,4-dichloro-2-butene. This compound contains 2 chlorine functional groups surrounding 2 carbons. This suggests that the addition of chlorine atoms has a larger impact on rejection than the addition of carbon atoms.



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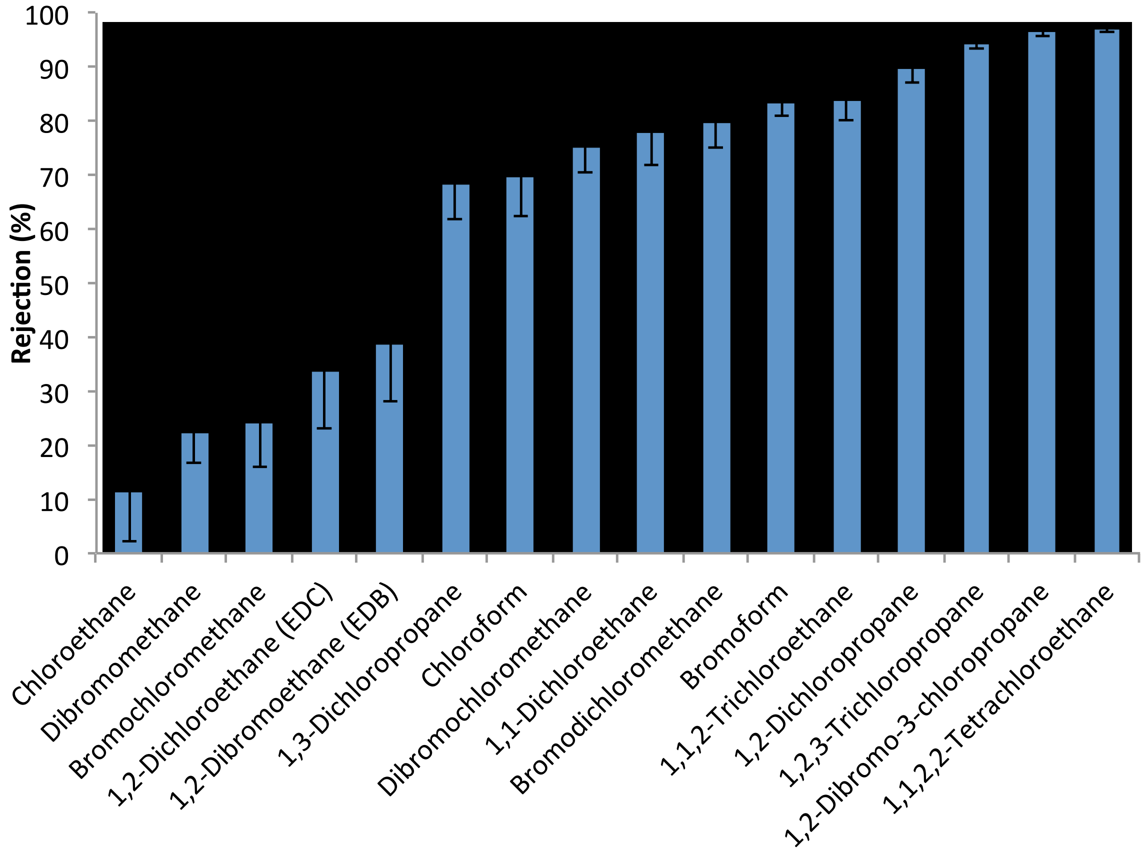
The haloalkenes containing three carbons and two chlorine atoms are seen in Figure 3.9. These three compounds are isomers of each other. The rejection of cis-1,3-dichloropropene and 1,1-dichloropropene are very similar. The rejection of trans-1,3-dichloropropene is about 20% lower than both compounds. The difference in the rejection of these compounds cannot be explained with the molecular weight and log K_{ow} values in Table 3.3. Therefore, a parameter describing the interaction of these compounds with the membrane material is needed to describe the differences in rejection between these three isomers.

3.7 Haloalkanes

Out of the 24 haloalkanes tested, 16 were included in the analysis. Figure 3.10 presents these compounds and their rejections. Rejection did not correlate well with either molecular weight nor log K_{ow} (Figure 3.11). Generally, however, as the number of halogen atoms increase, the rejections of the compounds also increase. The properties of each haloalkane are presented in Table 3.4.



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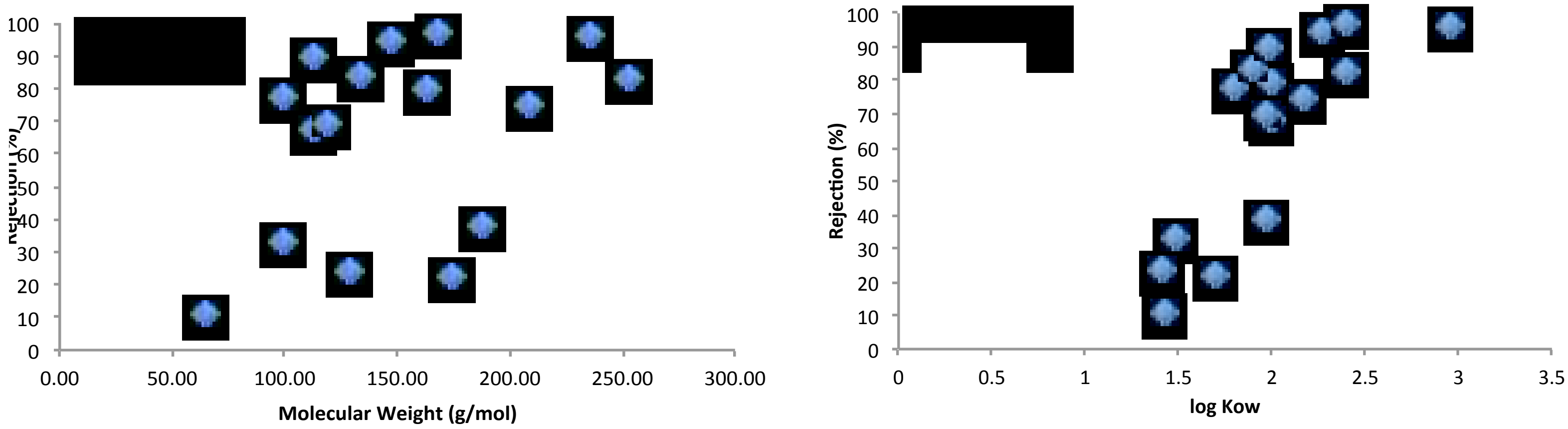

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Table 3.4: Molecular weight and log K_{ow} of the haloalkanes

Compounds	Molecular Weight (g/mol)	log K_{ow}
Chloroethane	64.51	1.43
Dibromomethane	173.84	1.70
Bromochloromethane	129.38	1.41
1,2-Dichloroethane (EDC)	98.96	1.48
1,2-Dibromoethane (EDB)	187.86	1.94
1,3-Dichloropropane	112.99	2.00
Chloroform	119.38	1.97
Dibromochloromethane	208.28	2.16
1,1-Dichloroethane	98.96	1.79
Bromodichloromethane	163.83	2.00
Bromoform	252.73	2.40
1,1,2-Trichloroethane	133.40	2.49
1,2-Dichloropropane	112.99	1.98
1,2,3-Trichloropropane	147.43	2.27
1,2-Dibromo-3-chloropropane	236.33	2.96
1,1,2,2-Tetrachloroethane	167.85	4.21

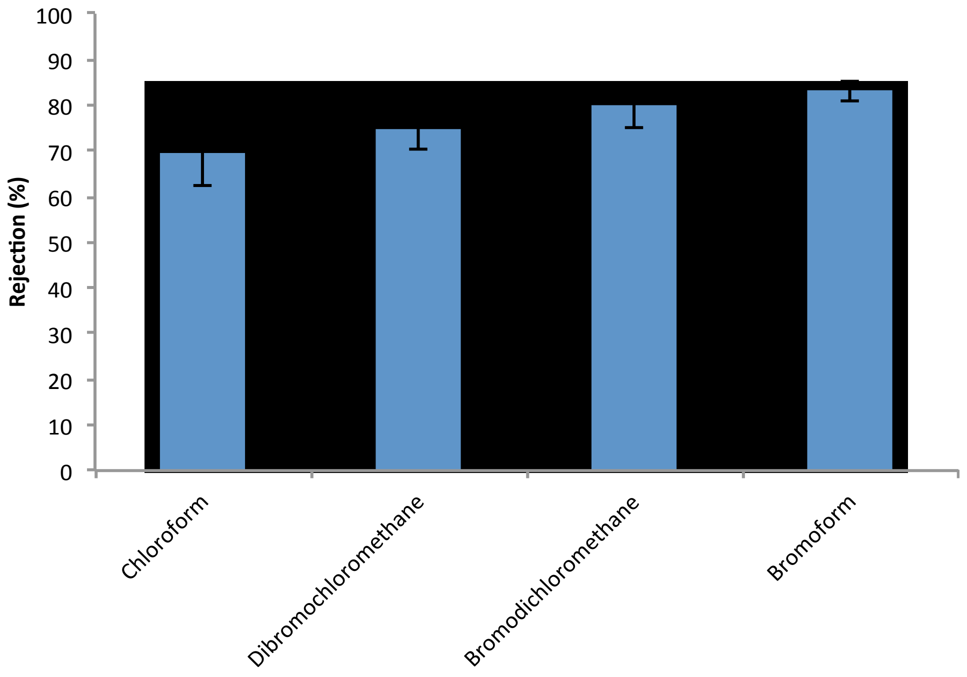
The haloalkanes containing two halogen atoms and one carbon are dibromomethane, and bromochloromethane. The rejections of dibromomethane and bromochloromethane are very similar, however, bromochloromethane has a slightly higher rejection of 5%. This difference, however, can be attributed to error associated with analytical error. It is expected that chloroethane has a rejection of over 20% lower rejection than both dibromomethane and bromochloromethane, as chloroethane has two carbons and one chlorine atom.

Three compounds contain two carbons and two functional groups; 1,1-dichloroethane, 1,2-dichloroethane, and 1,2-dibromoethane. The difference in rejection between 1,2-dichloroethane and 1,2-dibromoethane is only 5%, however, the expected trend of 1,2-dibromoethane being rejected higher was found. The two compounds of 1,1-dichloroethane and 1,2-dichloroethane are structural isomers. The difference in their rejections is 44%. This difference could be due to the increased molecular structural hindrance of 1,1-dichloroethane, as both chlorine functional groups are on the same carbon atom. A more detailed interaction parameter should be found, however, to describe this large difference in rejection.

The haloalkanes tested containing three carbon atoms and two functional groups are also is presented in Figure 3.10. These two compounds, 1,3-dichloropropane and 1,2-dichloropropane, are structural isomers of each other. The isomer containing more structural hindrance is 1,2-dichloropropane, considering the chlorine functional groups are located on carbons next to each other. This suggests that 1,3-dichloropropane can pass through the membrane easier, given it has about a 20% lower rejection than 1,2-dichloropropane. The difference in MW and K_{ow}, however, do not explain this large difference in rejection.

When comparing the di-haloalkanes, generally rejection increases as the number of carbon atoms increase. One exception to this trend is 1,1-dichloroethane. This compound contains two functional groups and two carbons, but is rejected about 10% higher than 1,3-dichloropropane, which contains two functional groups and three carbon atoms. This difference in rejection between these two compounds suggests that the chlorine molecules being on a longer chain of carbons in 1,3-dichloropropane could possibly allow the chlorine atoms access to react with the membrane material, leading to a lower rejection.

The tri-halo-methyl-alkanes tested were chloroform, dibromochloromethane, bromodichloromethane, and bromofom. The difference between each of these compounds is around 5%, as presented in Figure 3.12. Generally, compounds containing more bromine functional groups would be expected to have higher rejections due to the increase in molecular weight. This is the case when considering the difference in rejection of bromoform compared to chloroform, where bromoform also has a higher log K_{ow}. However, bromodichloromethane is rejected slightly higher than dibromochloromethane, despite the fact that dibromochloromethane has a higher molecular weight and log K_{ow}. This trend is similar to the trend between dibromomethane and bromochloromethane discussed above. Because this trend cannot be described with the two properties presented in Table 3.4, more research is needed to confirm these trends.



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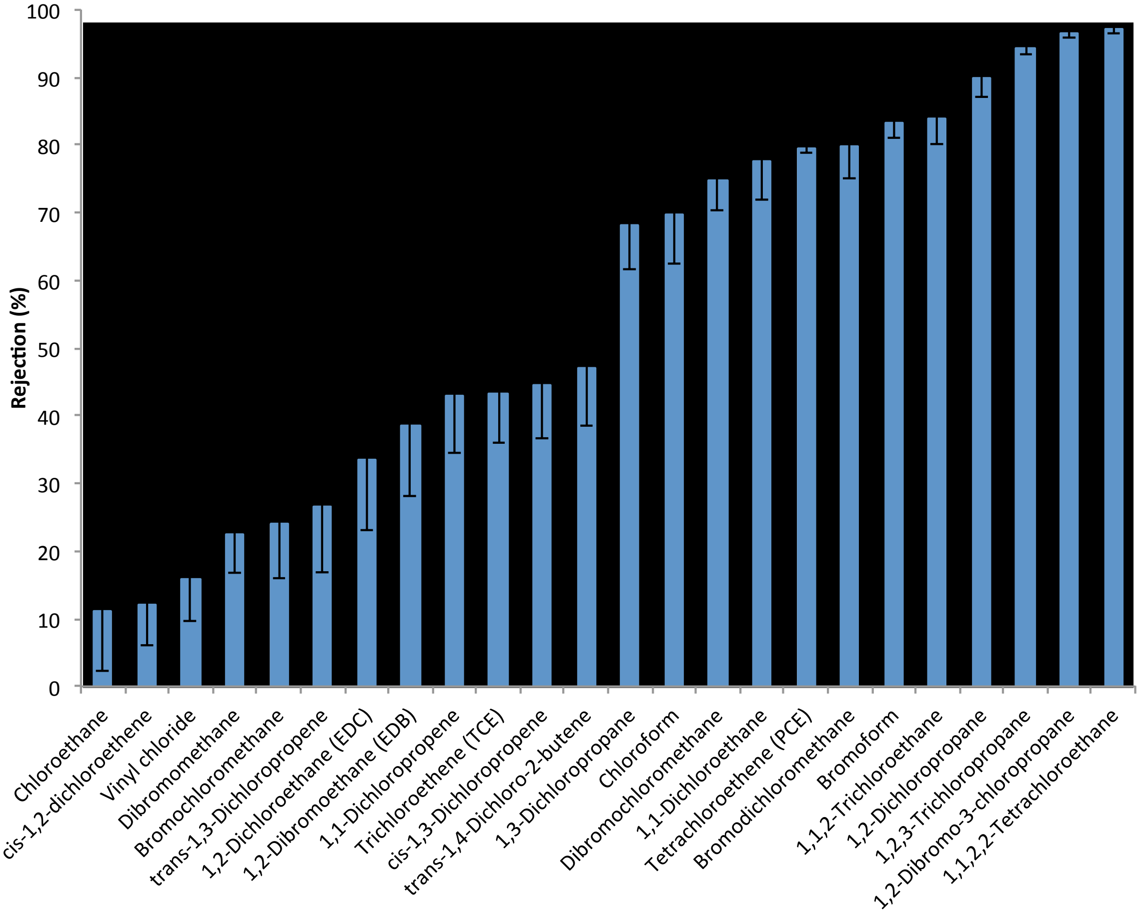
The compound with three chlorine atoms closest together is 1,1,1-trichloropropane, which has the highest rejection at 98%. Despite 1,2-dibromo-3-chloropropane having a higher molecular weight by about 100 g/mol, it has a slightly lower rejection than 1,1,1-trichloropropane, demonstrating the importance of a molecules structural hindrance on organics passage through RO membranes.

The only haloalkane containing four functional groups was 1,1,2,2-tetrachloroethane, which has the highest rejection at 97%. The compounds containing 3 functional groups and 2 or 3 carbons are 1,2-dibromo-3-chloropropane, 1,1,2-trichloroethane, and 1,2,3-trichloropropane. These compounds also have high rejections, with the lowest belonging to 1,1,2-trichloroethane at 83%. The difference in rejection between 1,1,2-trichloroethane and 1,2-3-trichloropropane is about 10%, which could be due to the increase in number of carbons between these two compounds. A higher log K_{ow} could also contribute to the difference in rejection between these two compounds.

3.8 Haloalkenes and Haloalkanes

Similar compounds between the haloalkenes and haloalkanes can be found. Figure 3.13 shows all haloalkane and haloalkene compounds versus their rejections. Generally, it can be seen that the haloalkenes experienced less rejection than the haloalkanes. Examples of this trend are described below with many of the similar compounds being compared in this section.



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Some of the simple haloalkane and haloalkene compounds are chloroethane, vinyl chloride, dibromomethane, and bromochloromethane. These compounds contain either one or two carbon atoms and halogen atoms. The 5% rejection difference between chloroethane and vinyl chloride can be due to large analytical errors of the two compounds. Both compounds have rejections less than 20%, which is to be expected since both compounds have low molecular weights around 60 g/mol. A larger difference in rejection can be seen when comparing vinyl chloride to dibromomethane and bromochloromethane, which is consistent with the suggestion that rejection is greater for higher molecular weight compounds. Although vinyl chloride has only one chlorine and weights 62.5 g/mol, it only has about a 10% lower rejection than bromochloromethane, which weights double vinyl chloride. Dibromomethane, which has a molecular weight of 173.8 g/mol, only has a slightly higher rejection than vinyl chloride. Furthermore, dibromomethane has a log K_{ow} of 1.70, compared to 1.62 for vinyl chloride. These two properties of dibromomethane being larger than vinyl chloride's properties lead to the expected higher rejection of dibromometane, but only by 7%. A larger difference between these compounds would be expected with the large difference in molecular weights between them. However, the large analytical errors need to be taken into account when comparing these compounds.

Two compounds with two chlorine atoms bonded to three carbons atoms are 1,1-dichloropropene and 1,2-dichloropropane. The difference in rejection between these two compounds is 47%, with 1,1-dichloropropene having the lower rejection of about 43%. This large difference in rejection could be due to the difference in the positions of the chlorine atoms. However, the double bond in 1,1-dichloropropene is most likely leading to its lower rejection.

This similar trend can also be seen between trans-1,3-dichloropropene and 1,3-dichloropropane. The difference in rejection between these compounds is about 40%, with 1,3-dichloropropane having the higher rejection of 68%. The double bond being present in trans-1,3-dichloropropene gives the molecule a much lower rejection. Even though trans-1,4-dichloro-2-butene contains four total carbons and two chlorines, compared to the three carbons and two chlorines of 1,3-dichloropropane, trans-1,4-dichloro-2-butene has a 21% lower rejection than 1,3-dichloropropane. This suggests that the presences of a double bond leads to a lower rejected compound more than molecular weight.

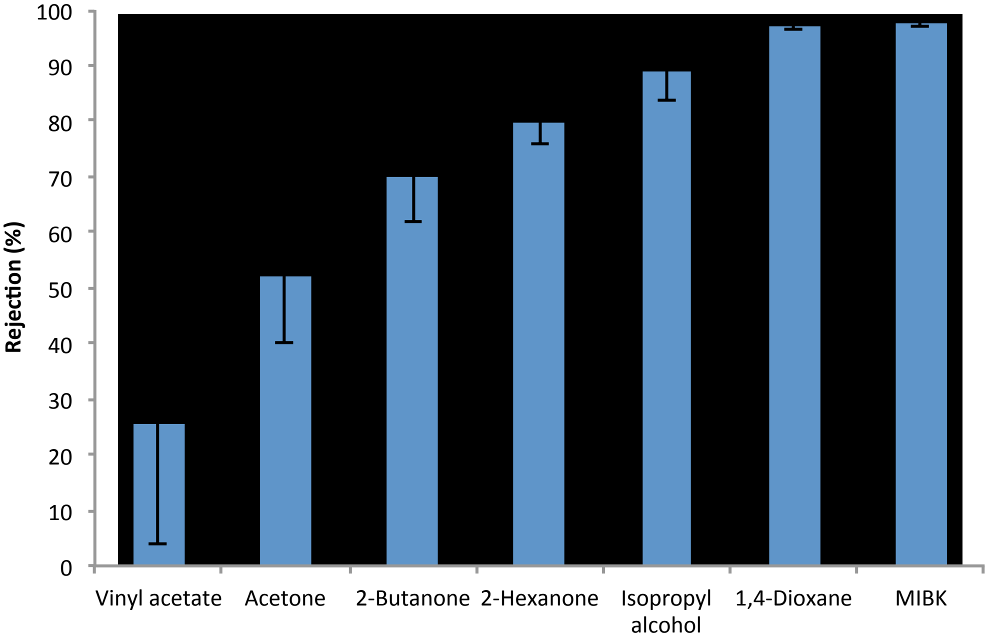
The difference in rejection between trichloroethene (TCE) and 1,1,2-trichloroethane is 40%. Both of these compounds contain three chlorine functional groups bonded to two carbon atoms. TCE has a higher molecular weight and log Kow than 1,1,2-trichloroethane. The lower rejection of TCE, about 43%, is due to the presents of the carbon double bond in the compound.

The two compounds with four chlorine atoms and two carbons in these two groups of compounds are tetrachloroethene (PCE) and 1,1,2,2-tetrachloroethane.

The difference in rejection, about 18%, is due to the presence of the double bond in PCE, as the molecular weights of these two compounds only differs by about 2 g/mol. Furthermore, the log K_{ow} of PCE is 3.4 compared to 1,1,2,2-tetrachloroethane's log K_{ow} of 2.39. If only considering the molecular weight and log K_{ow}, these two compounds rejection difference would not be able to be explained.

3.9 Oxygenated Compounds

Of the 12 oxygenated compounds tested, 7 gave data that met the criteria for analysis of their rejection. The results are summarized in Figure 3.14. Properties of the oxygenated compounds are presented in Table 3.5. Figure 3.15 presents the molecular weight and log K_{ow} the rejection of the oxygenated compounds. It can be seen that there is not a clear relationships between these molecular properties and the rejection for this group of compounds.



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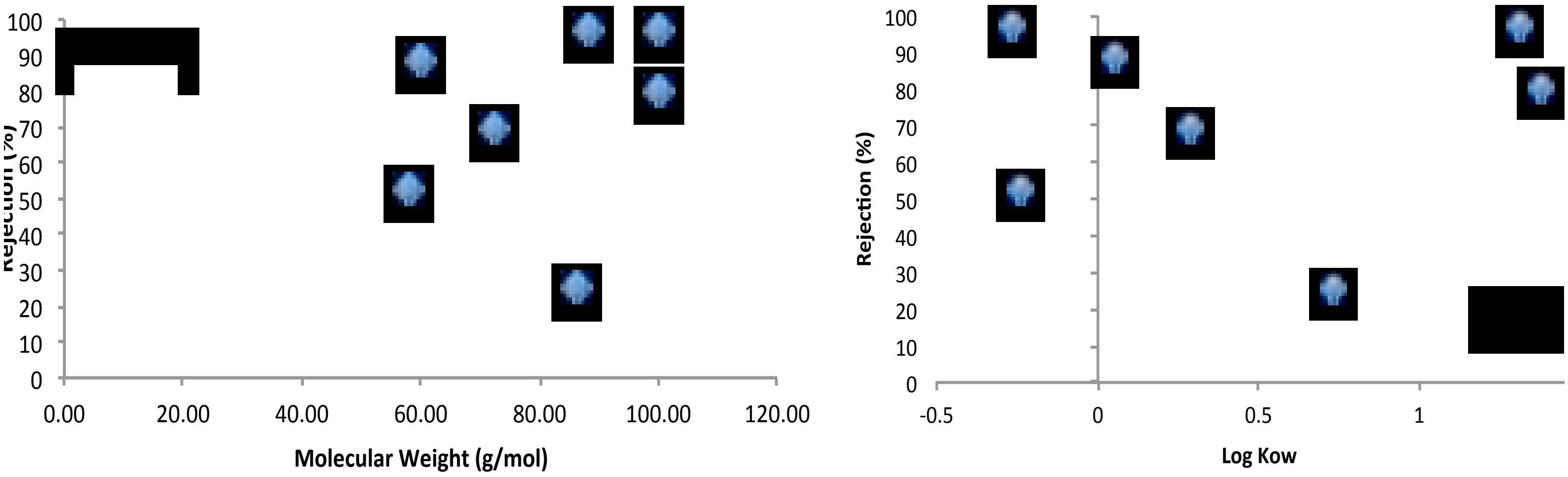

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Table 3.5: Molecular weight and log Kow for the oxygenated compounds

Compounds	Molecular Weight (g/mol)	log K_{ow}
Vinyl acetate	86.09	0.73
Acetone	58.08	-0.24
2-Butanone	72.11	0.29
2-Hexanone	100.16	1.38
Isopropyl alcohol	60.10	0.05
1,4-Dioxane	88.11	-0.27
4-methyl-2-pentanone (MIBK)	100.16	1.31

The two oxygenated compounds seen in Figure 3.14 with three carbons atoms are acetone and isopropyl alcohol. Acetone contains a carbonyl group, where isopropyl alcohol contains a hydroxyl group. These two compounds have nearly the same molecular weight. Isopropyl alcohol has a slightly higher log K_{ow}. However, isopropyl alcohol is rejected 36% higher than acetone, a large difference in rejection with only a slight difference in log K_{ow}. This difference in rejection could be due to the oxygen double bond in acetone interacting with the membrane material, causing it to diffuse through the membrane easier than isopropyl alcohol.

The four ketones tested were acetone, 2-butanone, 2-hexanone, and 4-methyl-2-pentanone (MIBK). For these compounds, the rejection increases with molecular weight. However, the two ketones with the same molecular weight are 2-

hexanone and MIBK. The structural difference between these two organic compounds is where the final methyl group is placed. The placement of the methyl group on the 4th carbon in MIBK makes this compound more "bulky" than 2-hexanone, where the methyl group is placed on the 5th carbon. This suggests that since MIBK has a rejection of 17% higher than 2-hexanone, structural hindrance could be an important factor governing the higher rejection of MIBK.

Vinyl acetate's properties can be seen in Table 3.5. With these two properties, vinyl acetate would be expected to have a rejection between 2-butanone and 2-hexanone, as both properties are in-between the two ketones. Instead, vinyl acetate is rejected the lowest of all compounds tested in the oxygenated group, with much error in its rejection. This could possibly suggest that with the two oxygen compounds and the two carbon double bonds, the mass transfer through the membrane is very high. However, the error when analyzing vinyl acetate could be the reason for this trend seen.

3.10 Conclusions

RO rejection experiments were completed on a wide range of organic compounds with varying functional groups. These compounds make up 5 different groups of organics discussed above; halobenzenes, alkylbenzenes, haloalkenes, haloalkanes, and oxygenated compounds. These organic compounds were chosen based on their different functional groups in order to gain insight into how changes in functional chemistry affect organic rejection through RO membranes.

The three general rejection mechanisms accepted by industry are size, electrostatic repulsion, and adsorption to the membrane. The molecular properties used to describe these mechanisms were molecular weight and log K_{ow}. While these properties could describe general trends in the organics rejection in some cases, other trends could not be explained by these molecular properties alone.

The difference in the isomers rejections discussed above provides good insight into the need to look closely at the chemistry of the functional groups in a given molecule to understand its rejection. While properties for isomers are the same, often large differences in rejection between them was seen. Generally, the closer (spatially) together the functional groups, the higher the rejection. This trend is possibly due to the molecule's structure having an impact on the ability for the molecule to interact with the membrane material. The only exception to this trend is the difference between the two trimethylbenzene isomers; 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene. The difference in the rejection between these two compounds was only about 3%. This very slight difference, and therefore exception to this general trend between all other groups of structural isomers, could be due to the very large size of 1,3,5-trimethylbenzene.

It was generally observed that when comparing compounds containing methyl groups to halogens, the compounds containing methyl groups were rejected higher. This could be due to the larger volume of the methyl group compared with a halogen, suggesting molecular weight may not be the best property to use to explain the rejection mechanism of size exclusion. Also generally observed is that compounds containing hydroxyl functional groups are rejected higher than compounds containing carbonyl functional groups. An example of this observation is between isopropyl alcohol and acetone, where isopropyl alcohol has a 36% higher rejection than acetone.

When comparing compounds with the same number of functional groups, as the number of carbons in each molecule increases, rejection was also generally observed to increase. With respect to molecular weight and log K_{ow}, this observation was expected. Differences in the rejection of most of the alkylbenzenes are examples of this trend. As the number of carbons in the alkyl functional groups increased, the rejection also increased for these compounds. However, some exceptions to this general trend exist. The difference in rejection between 1,3-dichloropropane and 1,1-dichloroethane is an example of an exception to this general trend.

Another general trend observed was as the number of functional groups on each molecule increased, the rejection also increased. This trend can be explained by the increased molecular weight in compounds containing more functional groups leading to an increased rejection.

The presence of a carbon-carbon double bond in a molecule leads to a lower rejection of that molecule. Many examples of this trend can be seen in Section 3.8, where the differences in rejection between the haloalkane and haloalkene compounds tested was discussed. The difference in rejection between acetone and isopropyl alcohol demonstrates this trend again, with isopropyl alcohol having a larger rejection than acetone by 36%.

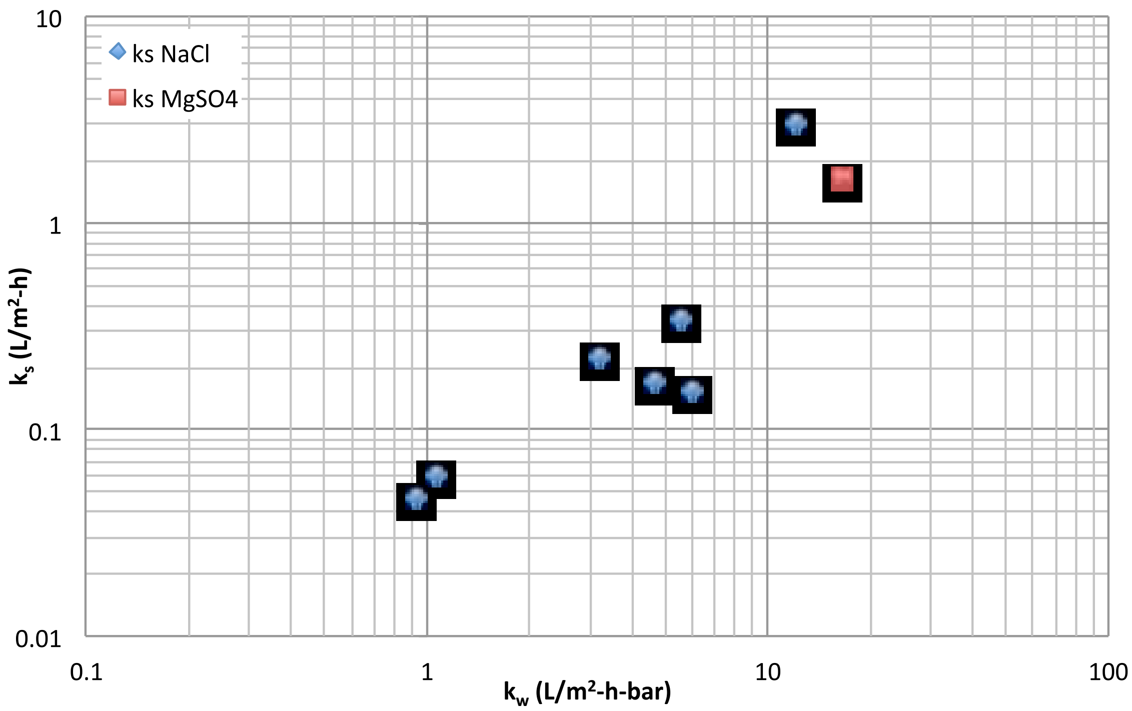
A trend describing the difference in rejection between compounds containing alkyl functional groups is the more branching in the molecule , the higher the rejection. This trend can be seen between 2-hexanone and MIBK, which are two oxygenated compounds with the same molecular weight and very similar log K_{ow} values. Despite the similarities in molecular properties, MIBK has a 17% higher rejection than 2-hexanone. Two other examples of this trend are between four of the alkylbenzenes. N-propylbenzene and isopropylbenzene both contain three carbons in their alkyl functional groups, however, n-propylbenzene is rejected 11% lower than isopropylbenzene. Both n-butylbenzene and sec-butylbenzene have four carbon atoms in their alkyl functional groups. The rejection of n-butylbenzene is about 9% less than sec-butylbenzene, where sec-butylbenzene contains the more branched alkyl functional group.

3.11 Discussion

Due to the fact that the properties used in this study, molecular weight and log K_{ow}, did not correlate well with the differences in rejection for some compounds, further studies need to be completed to develop an explanation for the differences in rejection. The use of one property, however, is not likely to describe the differences in rejection. Instead, a property that describes the interaction of each molecule with the membrane material would be more efficient. An interaction coefficient could be calculated based on all properties of a molecule. For the WateReuse Research Association (WRRF) project 14-19, this idea is currently being investigated by a research team at Michigan Technological University (MTU). The team is attempting to use the aqueous-phase free energy of interaction to describe the interaction of the organic compounds with the poly-amide (PA) membrane material. This interaction coefficient would describe the differences in a molecules ability to interact with the membrane material, which ultimately determines the molecules rejection.

4. Boron Model to Predict Organics Rejection

As discussed in Chapter 2, the water and solute mass transfer coefficients were calculated based on the membrane manufacturer's test conditions on the specification sheet for each membrane. A linear relationship between each membrane's k_w and k_s of sodium chloride (k_{NaCl}) is plotted in Figure 4.1. The k_s for the NF 270 is presented in Figure 4.1 as the k_s for $MgSO_4$, as the manufacturer does not report a value for NaCl. As a result, a linear relationship between the k_W and the k_s of other solutes, more specifically organic compounds, was hypothesized after this initial relationship was observed. Figure 4.2 shows the observed relationship between the experimental values of k_W and the k_s of boron and other well-known organic compounds for each of the 8 membranes used in experiments. Each organic has a trend with k_W similar to that initially observed between NaCl and k_W. By determining the slope of each trend line between the k_W and organic k_s ($k_{Organics}$) and knowing k_s values for one membrane, the organics mass transfer through other membranes could be predicted. By knowing the k_W, or another membrane descriptor for any membrane, it is suggested that a model could be created to predict the rejection of organics through any membrane. The membrane descriptor is what will be used to describe the independent variable in the model development.



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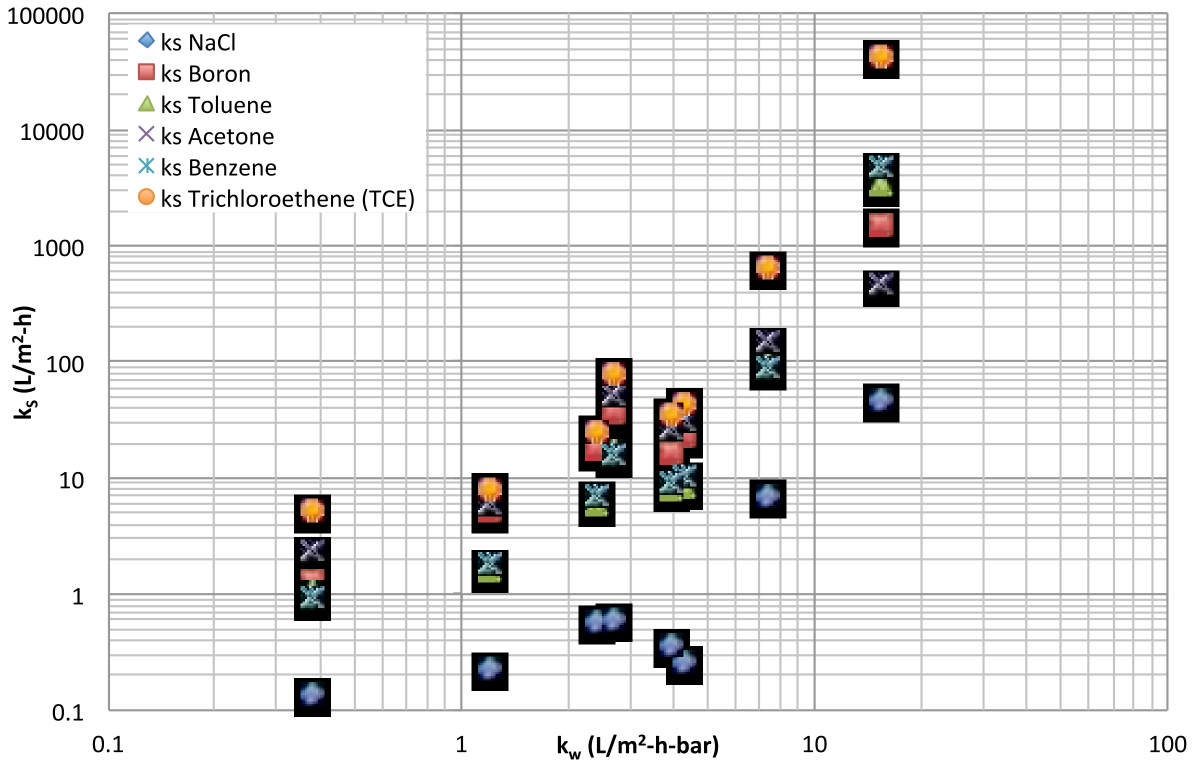
The objective of this section was to create a linear regression model to predict the organic rejection between different RO membrane products. This was done by first choosing a membrane as a reference membrane. Then, either a membrane descriptor (k_W) or a compound's mass transfer coefficient (k_S) were chosen as the dependent variable in the linear regression model.



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4.1 Model Development

The model was developed by first analyzing each molecule's k_S value for NaCl through each membrane, except the Dow Filmtec NF 270, which will be discussed later. The Hydranautics ESPA2-LD and Toray TM800M were tested in the first and last cell in the system, providing duplicate measurements for those two membranes. At the lowest test pressure for each membrane group, the last membrane in the series was sampled in triplicate measurements. This gave the Hydranautics ESPA2-LD and Toray TM800M 8 calculated k_S values to compare to each other. The other five membranes tested had 3 separate k_S values for comparison. Although the k_S values were determined at different operating pressures, the solution/diffusion model suggests that the k_s value should be a constant for each organic through each membrane; therefore, the k_s values can be treated as replicates. The k_s values were compared to each other by taking the relative standard deviation (RSD) of the k_s measurements for each organic. If the RSD was calculated to be 0.5 or greater, that compound was considered to have poor repeatability and was no longer considered in the model development.

The Hydranautics ESPA2-LD membrane was used as the reference membrane for model development. This membrane was chosen due to its wide use in the potable reuse industry. Because the ESPA2-LD membrane was used as the reference membrane for the model, any compounds with an RSD value of 0.5 or above for the ESPA2-LD membrane were not used in the model.

The Dow Filmtec NF270 membrane was not used in model development. This membrane rejected nearly all of the organics poorly, and had very low experimental NaCl salt rejection of 53%. Due to this membrane being a nanofiltration membrane, its rejection mechanism is different than for RO membranes (Steinle-Darling et al., 2010). Furthermore, the NF 270 would not be allowed for use in potable reuse facilities in the state of California due to requirements that the average sodium chloride rejection be no less than 99.2% for any RO membrane being used in the advanced treatment train. The stated typical stabilized $MgSO_4$ rejection on the NF 270 specification sheet is >97%, making this membrane not eligible to use in water reuse facilities (California Department of Health Title 22, Article 5.2, 2014).

The inputs into the linear regression analysis are the k_w for each membrane, and the $k_{Organic}$ for the ESPA2-LD membrane. An initial guess for the slope, chosen based on the calculated average slope for all the organic compounds and boron, was used to start the optimization process. The output of the model is the $k_{Organic}$ for the other RO membranes. The error of the model was calculated by taking the square of the measured $k_{Organic}$ values minus the predicted $k_{Organic}$ for each organic, as described in Equation 4.1. The method of least squares was then used to minimize the error in the linear regression model. These squared errors of each organic for the individual membranes were then summed, as presented in Equation 4.3 The slope was optimized by minimizing the summed error by using Solver in Microsoft Excel. By first predicting the $k_{Organic}$ for the membranes using the linear regression model, the rejection for each organic could then be calculated using Equation 4.2 The medium pressure test data was used in Equation 4.2, which is presented in Table 4.1. The log $k_{Organic}$ values for the ESPA2-LD membrane and the log $k_{Organic}$ used for each other membrane are presented in Table 4.2.

Using the developed model for any organic would require the use of Equation 4.4. The inputs into the linear regression model are the k_w, or membrane descriptor, for each membrane, and the $k_{Organic}$ for the ESPA2-LD membrane. The output of the model is a $k_{Organic}$ value for the membrane in question.

$$\log(k_{Organic}) = m \cdot log(k_W) + b \qquad \textbf{Equation 4.1}$$

$$Rej_{Predicted}\ (\%) = \frac{1}{\frac{k_S \beta_0}{J_W} + 1} \qquad \textbf{Equation 4.2}$$

$$Error = (\log\,(k_{Org,Predicted}) - \log\,(k_{Org,Measured}))^2 \qquad \textbf{Equation 4.3}$$

$$\log(k_{Organic}) = m \cdot log(k_w - k_{W,ESPA2-LD}) + log(k_{Organic,ESPA2-LD}) \qquad \textbf{Equation 4.4}$$

Table 4.1: Medium pressure data for model development

Membrane	Concentration Polarization Factor	J_w (L/m^{2}h)
ESPA2-LD	1.25	43.65
TMG(D)	1.14	24.70
BW30XFRLE	1.23	39.69
AG LF	1.15	27.02
TM800M	1.16	28.61
SW30XHR	1.06	8.97

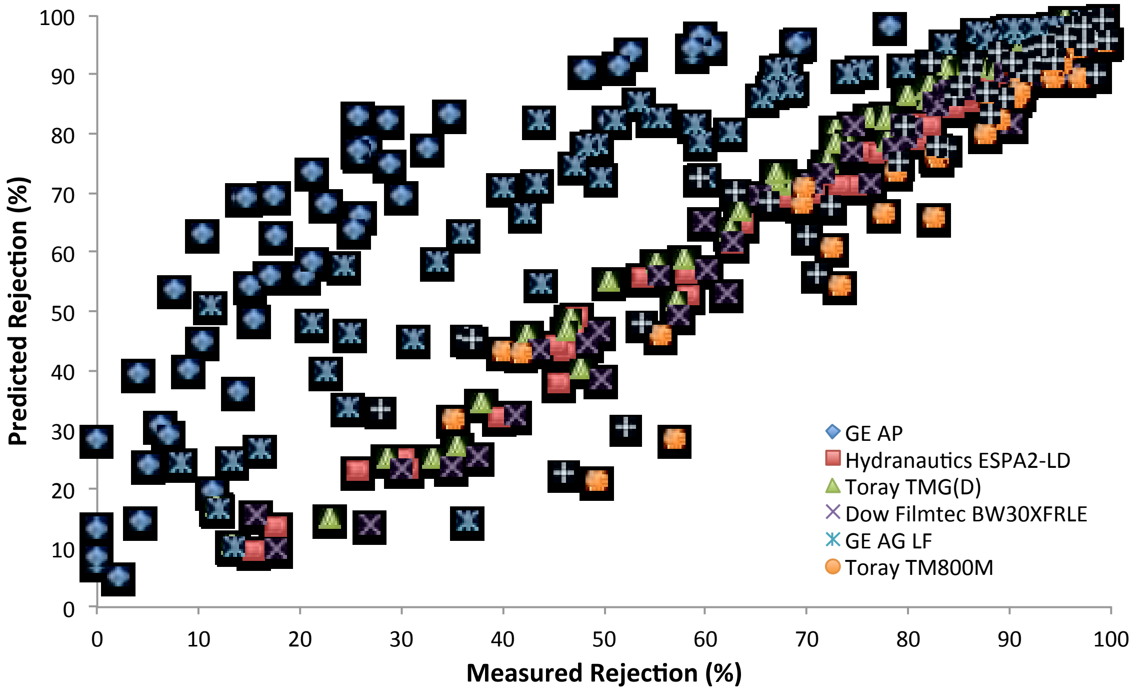
Table 4.2: All log $k_{Organic}$ values used in model

Compounds	log $k_{Organic}$						
	AP	ESPA2-LD	TMG(D)	BW30XFRLE	AG LF	TM800M	SW30XHR
1,1-Dichloroethane	1.99	0.96	0.91	1.00	1.21	0.31	0.02
1,1-Dichloropropene	2.65	1.66	1.41	1.60	1.71	0.78	0.66
1,1,2-Trichloroethane	1.88	0.78	0.71	0.87	1.10	0.15	-0.07
1,1,2,2-Tetrachloroethane	1.29	-0.01	0.21	0.12	0.44	-0.30	-0.55
1,2-Dibromo-3-chloropropane	1.50	0.07	0.26	0.20	0.55	-0.30	-0.51

1,2-Dibromoethane (EDB)	2.81	1.76	1.47	1.66	1.99	1.00	0.66
1,2-Dichlorobenzene	2.20	0.90	0.83	0.99	1.30	0.22	-0.13
1,2-Dichloroethane (EDC)	2.63	1.87	1.62	1.78	1.93	1.00	0.64
1,2-Dichloropropane	1.76	0.56	0.56	0.64	0.81	0.01	-0.25
1,2,3-Trichlorobenzene	1.96	0.57	0.52	0.62	1.04	-0.28	-0.80
1,2,3-Trichloropropane	1.53	0.27	0.34	0.40	0.67	-0.18	-0.43
1,2,4-Trichlorobenzene	2.35	1.02	0.84	0.99	1.37	-0.06	-0.76
1,2,4-Trimethylbenzene	1.33	0.11	0.17	0.23	0.41	-0.51	-0.80
1,3-Dichlorobenzene	2.62	1.19	1.06	1.27	1.59	0.52	0.05
1,3-Dichloropropane	2.27	1.18	1.03	1.16	1.50	0.54	0.27
1,3,5-Trimethylbenzene	0.90	-0.50	-0.02	-0.31	-0.14	-0.72	-0.99
1,4-Dichlorobenzene	2.97	1.44	1.26	1.48	1.84	0.71	0.28
1,4-Dioxane	NA	-0.05	0.28	-0.12	0.37	-0.39	-0.72
2-Butanone	2.02	1.15	1.06	1.08	1.33	0.52	0.11
2-Chlorotoluene	1.94	0.71	0.67	0.81	1.06	0.01	-0.26
2-Hexanone	1.76	0.90	0.80	0.78	1.20	0.11	-0.23
4-Chlorotoluene	2.26	1.28	1.11	1.34	1.54	0.49	0.13
4-Isopropyltoluene	1.31	-0.19	-0.05	-0.09	0.11	-0.73	-1.14
4-Methyl-2-pentanone	1.09	-0.09	0.13	-0.09	0.26	-0.40	-0.70
Acetone	2.18	1.49	1.40	1.42	1.72	0.78	0.37
Benzene	1.96	1.01	0.86	0.96	1.21	0.26	-0.03
Bromobenzene	2.42	1.43	1.17	1.43	1.71	0.72	0.34
Bromochloromethane	2.77	2.06	1.89	1.95	2.40	1.72	1.32
Bromodichloromethane	2.30	0.91	0.84	0.93	1.34	0.46	0.19
Bromoform	2.04	0.81	0.73	0.88	1.31	0.26	0.07
Chlorobenzene	2.47	1.34	1.11	1.29	1.64	0.59	0.43
Chloroethane	2.74	2.34	1.81	2.59	2.14	1.25	0.94
Chloroform	2.18	1.15	1.02	1.17	1.43	0.50	0.20
cis-1,2-DCE	3.14	2.51	2.06	2.26	2.20	1.48	1.07
cis-1,3-Dichloropropene	2.88	1.61	1.42	1.54	1.97	1.09	0.78
Dibromochloromethane	2.09	1.03	0.90	1.08	1.39	0.41	0.20
Dibromomethane	2.85	2.06	1.85	1.98	2.51	1.59	1.27
Ethylbenzene	1.92	0.74	0.64	0.79	1.05	0.08	-0.11
Isopropyl alcohol	1.46	0.59	0.67	0.65	0.91	0.04	-0.33
Isopropylbenzene	1.32	0.02	0.33	0.16	0.54	-0.45	-0.72
mp-Xylenes	1.78	0.71	0.63	0.75	1.03	0.01	-0.17
n-Butylbenzene	NA	0.61	0.28	0.40	0.88	-0.83	-1.46
n-Propylbenzene	1.92	0.72	0.62	0.80	1.03	-0.06	-0.57
Naphthalene	1.90	0.59	0.52	0.59	1.04	0.02	-0.34
o-Xylene	1.45	0.23	0.27	0.30	0.52	-0.37	-0.56
sec-Butylbenzene	1.14	-0.05	0.04	0.01	-0.03	-0.60	-0.96
Styrene	2.05	1.11	0.91	1.09	1.41	0.40	0.23
Tetrachloroethene (PCE)	2.22	0.91	0.93	1.03	1.45	0.35	0.28
Toluene	1.99	0.92	0.78	0.90	1.23	0.21	0.03
trans-1,3-Dichloropropene	3.06	2.02	1.68	1.85	2.24	1.34	0.97
trans-1,4-Dichloro-2-butene	NA	1.56	1.35	1.45	2.23	1.05	0.85
Trichloroethene (TCE)	2.82	1.64	1.41	1.56	1.89	0.91	0.73
Vinyl chloride	NA	2.28	2.27	2.28	2.58	1.71	1.51

4.2 Using k_w as the Membrane Descriptor

Figure 4.3 presents the comparison between the experimental or measured rejection values and the rejection predicted using the linear regression model created with each membrane k_w value as the membrane descriptor, as described in Equation 4.1. The optimized slope in Equation 4.4 was found to be 0.994.



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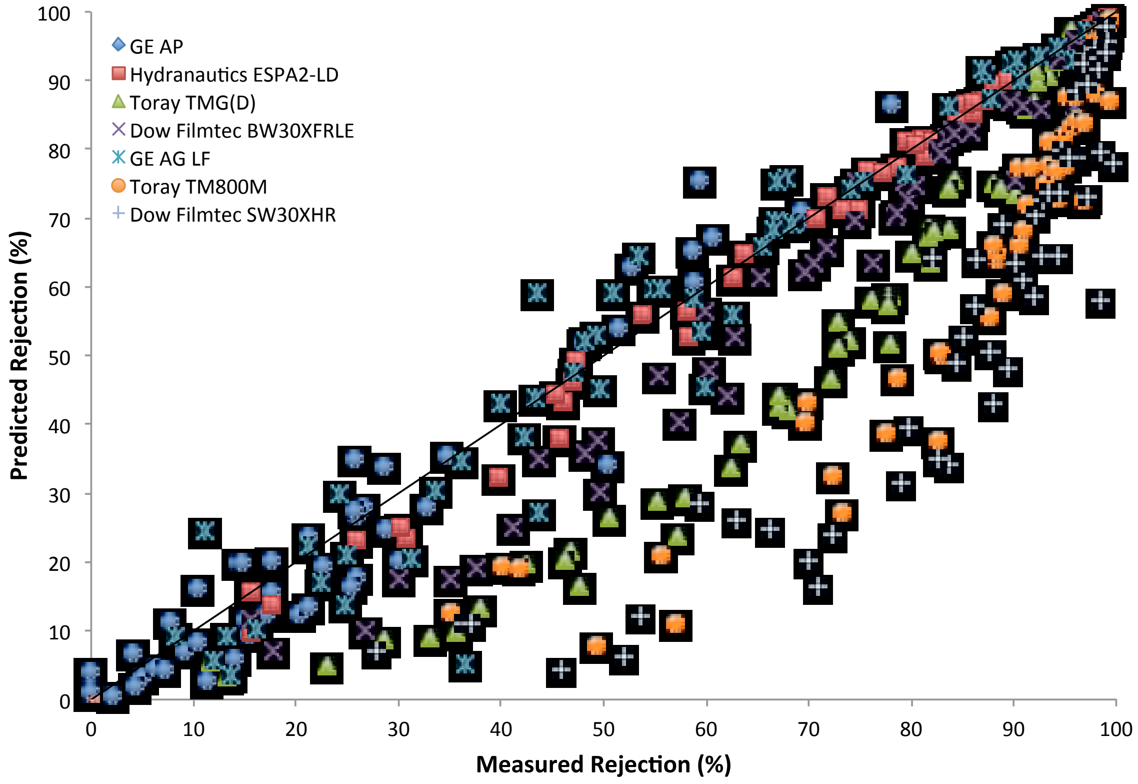
Despite the fact that NaCl and the other organics have linear relationships with the water mass transfer coefficient, presented in Figure 4.1 and 4.2, using the k_w as a membrane descriptor to predict the organics transfer through each membrane did not create an accurate model. This suggests that the membrane material's interaction with water for passage through the membrane is different than the interaction of the organics with the membrane material. Generally the rejection of organics by the GE AP and GE AG LF membranes are over predicted, while the rejection of organics by the TM800M is under predicted using k_w. There are also large errors in the predicted $k_{Organic}$ values for all membranes at the low rejections.

4.3 Using Mass Transfer Coefficient for NaCl as the Membrane Descriptor

The rejection of NaCl is a parameter that membrane manufacturer's provide on RO membrane specification sheets. It was hypothesized that since the k_w of each membrane did not provide a an accurate correlation for rejection of the organics, the NaCl mass transfer coefficient could be used instead. Equation 4.5 shows the linear regression model with log k_{NaCl} used in place of k_w. Figure 4.4 presents the measured rejection versus the predicted rejection using the K_{NaCl} as the membrane descriptor.

$$\log(k_{Organic}) = 0.830 \cdot log(k_{NaCl} - k_{NaCl,ESPA2-LD}) + log(k_{Organic,ESPA2-LD}) \quad \textbf{Equation 4.5}$$



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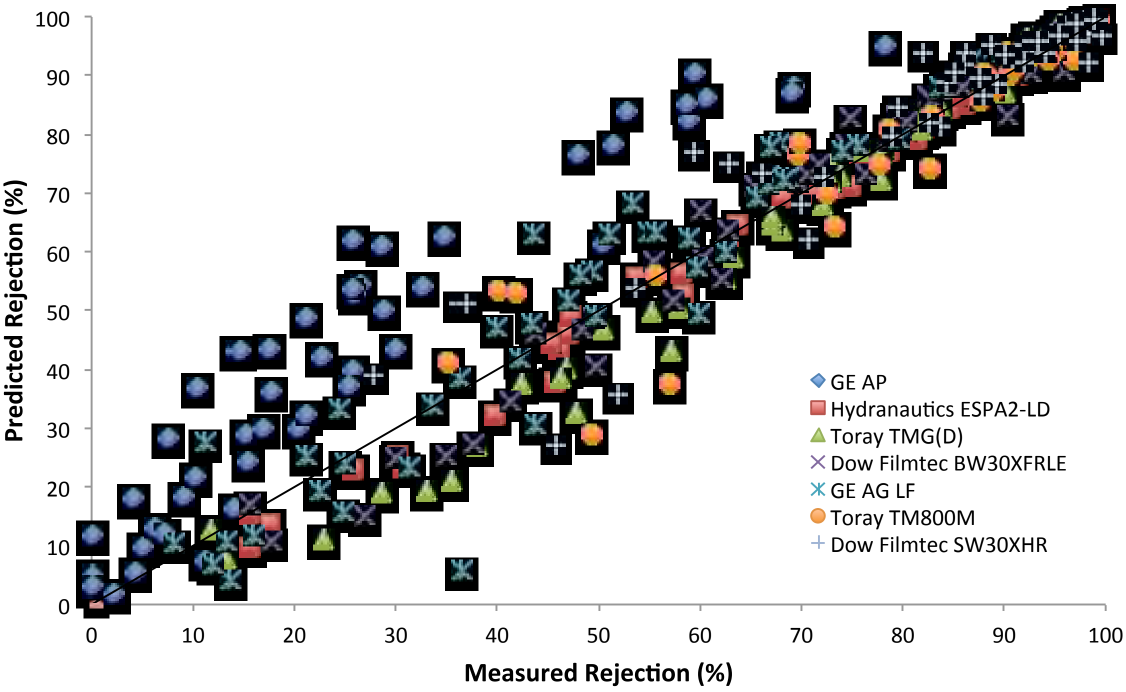
NaCl has very high rejection through all of the RO membranes tested. The NaCl rejections were found to be high compared to most organics, which leads to an under-prediction of rejection of organics by all membranes. The under prediction of all organic rejections by the membranes suggests that, as expected, the rejection mechanisms for NaCl and the neutral organics is different. Once NaCl dissociates in water, it becomes two monovalent ions. The mechanism for rejection for small, charged ions is electrostatic repulsion (Bellona et al., 2004). The low molecular weight organics tested are neutral at the pH used in experiments. Therefore, they are not rejected based on electrostatic exclusion, but by other rejection mechanisms. This could be the explanation as to why the mass transfer coefficient for NaCl had a poor correlation to rejection of the organic compounds.

4.4 Using Mass Transfer Coefficients for Organic Compounds as the Membrane Descriptor

Due to the fact that the NaCl mass transfer coefficients did not provide good model results, the use of a neutral and low-rejected compound for the input of the model was then considered. Both the mass transfers of acetone and benzene were evaluated as the membrane descriptor input. Equations 4.6 and 4.7 show the linear regression models using the mass transfer of acetone and benzene as the membrane descriptors. Figures 4.5 and 4.6 shows the measured versus predicted rejections for each organic and membrane tested using $k_{Acetone}$ and $k_{Benzene}$.



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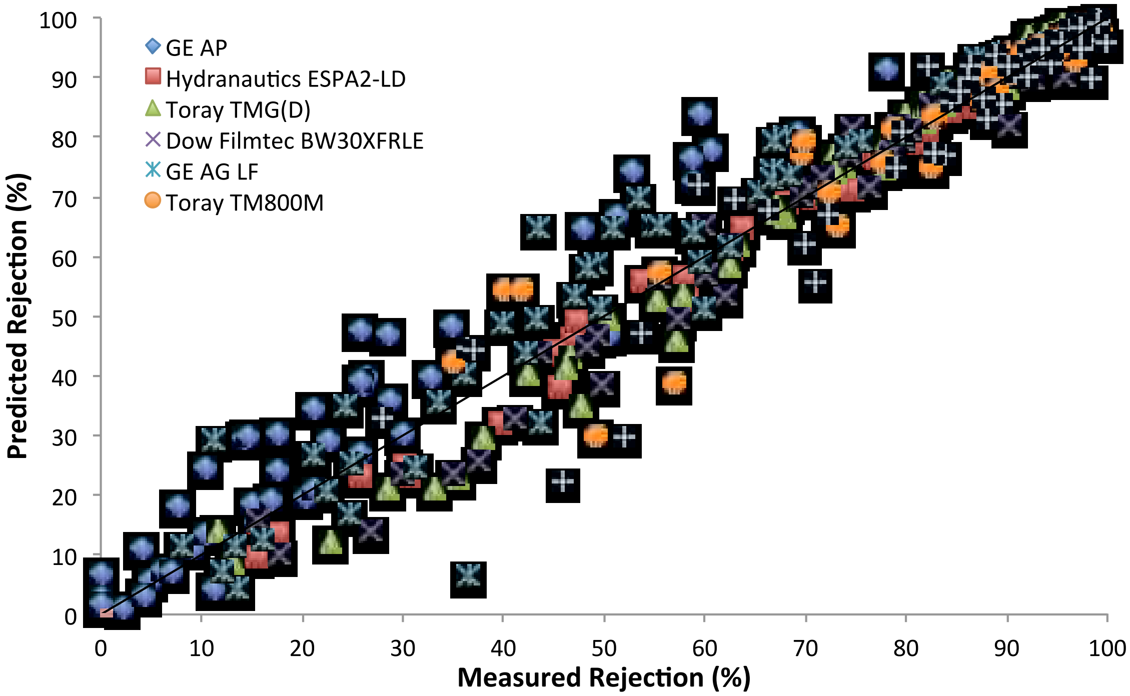
$$\log(k_{Organic}) = 1.02 \cdot log(k_{Acetone} - k_{Acetone,ESPA2-LD}) + log(k_{Organic,ESPA2-LD})$$

Equation 4.6

$$\log(k_{Organic}) = 0.999 \cdot log(k_{Benzene} - k_{Benzene,ESPA2-LD}) + log(k_{Organic,ESPA2-LD})$$

Equation 4.7



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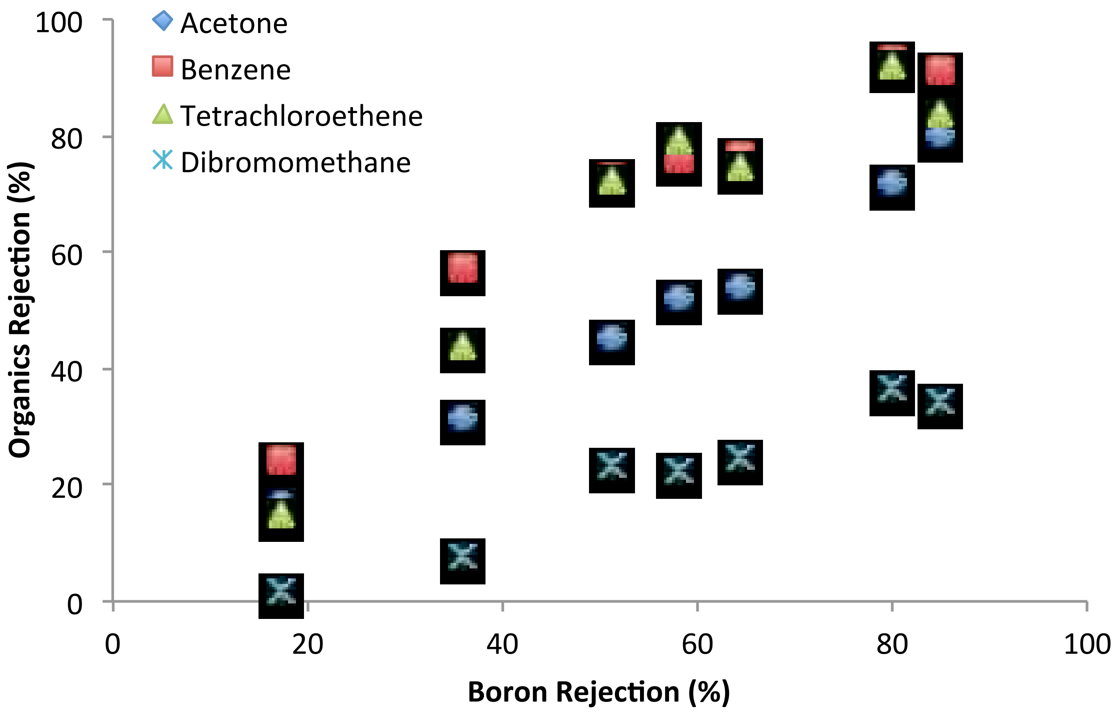
Using the $k_{Acetone}$ and $k_{Benzene}$ as the membrane descriptor in each attempted model provided a more accurate model than using either k_w or k_{NaCl}. However, the compound chosen as the reference compound for model development should be a compound that membrane manufacturers list it on their specification sheets, similar to the sodium chloride rejection. This should be done so the specifications provide a better measure of the membrane's ability to remove low molecular weight organic compounds. . The use of an organic compound as the reference compound for the model would require membrane manufacturers to test the chosen reference compound with their membranes to provide the rejection of that compound on their specification sheets.

4.5 Using Mass Transfer Coefficient for Boron as the Membrane Descriptor

Membrane manufacturers already include boron rejection on some membrane specification sheets, specifically for their seawater membranes. Boron can be harmful to plants and crops, which is an issue for places using desalinated water for irrigation. Since information is already available regarding boron rejection of seawater membranes, it was hypothesized that boron could serve as a good reference compound for this model. If membrane manufacturers place boron rejections on the specification sheets for all membranes, then boron rejection would not need to be tested by researchers or utilities for use in this model.

The rejection of boron ranges between 17-85% for seven of the membranes tested. It generally has a low rejection because it is a small molecule that is present as neutral boric acid near neutral pH. Furthermore, boron has a low molecular weight of 61.83 g/mol. Boron is not a volatile compound as are low molecular weight organic compounds, making it easier to work with in the lab. Further, analysis of boron is easier than for organics. For these reasons, boron offers advantages over sodium chloride and organic compounds for use as the reference compound in this model.

Finally, boron was found to correlate well with NDMA in a previous study. Tu et al. (2013) tested boron and NDMA rejection through six different membrane products at various operating conditions. They found that boron had a strong linear correlation with NDMA rejection, with an R^2 value of 0.95. Figure 4.7 below presents



[redacted]

the rejection of boron versus organic compounds rejection used in this study. A similar strong linear trend can be found with the 7 tested membranes in this study, with R^2 values shown for each organic in Table 4.3. The slope for each linear trend-line between boron and the organics shown in Figure 4.7 is presented in Table 4.3.

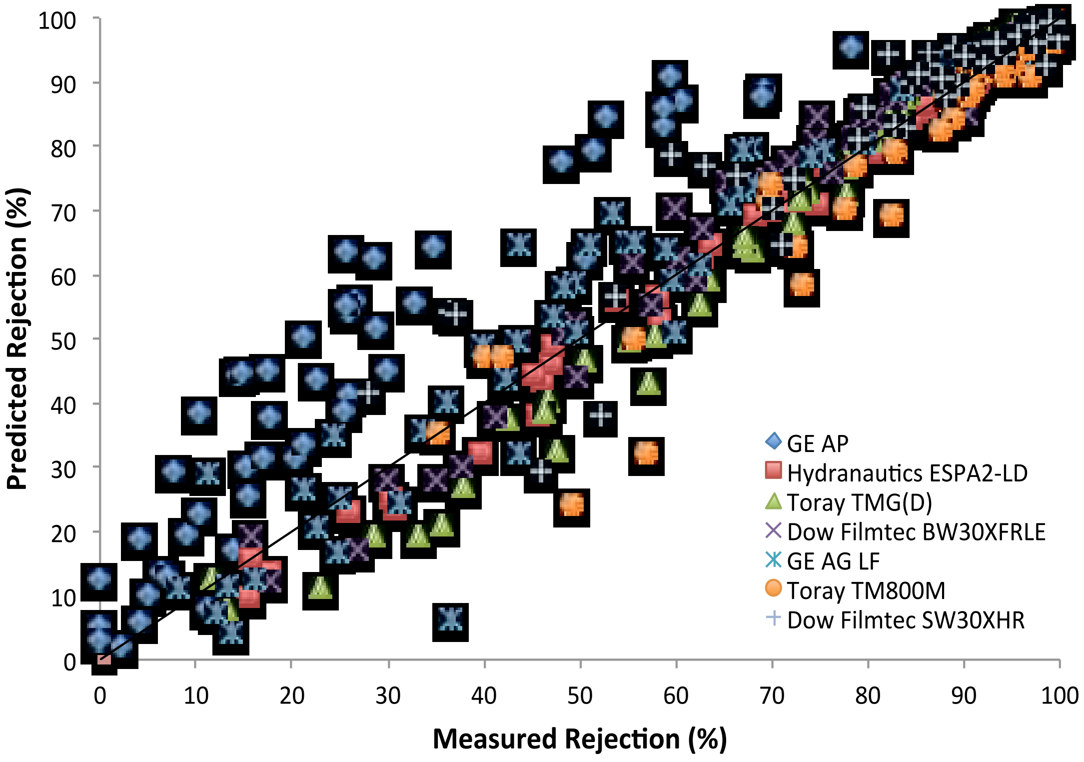
Table 4.3: Slope and R^2 values for organics linear correlation with boron

Organic	Organic Group	Slope	R^2
Acetone	Oxygenated	0.91	0.99
Benzene	Aromatic	0.95	0.93
Tetrachloroethene	Haloalkene	1.07	0.88
Dibromomethane	Haloalkane	0.53	0.95

Equation 4.8 shows the linear regression model using the k_{Boron}. Figure 4.8 presents the measured versus predicted rejection for each organic and membrane tested using the k_{Boron} as the membrane descriptor.

$$\log(k_{Organic}) = 0.959 \cdot log(k_{Boron} - k_{Boron,ESPA2-LD}) + log(k_{Organic,ESPA2-LD})$$

Equation 4.8



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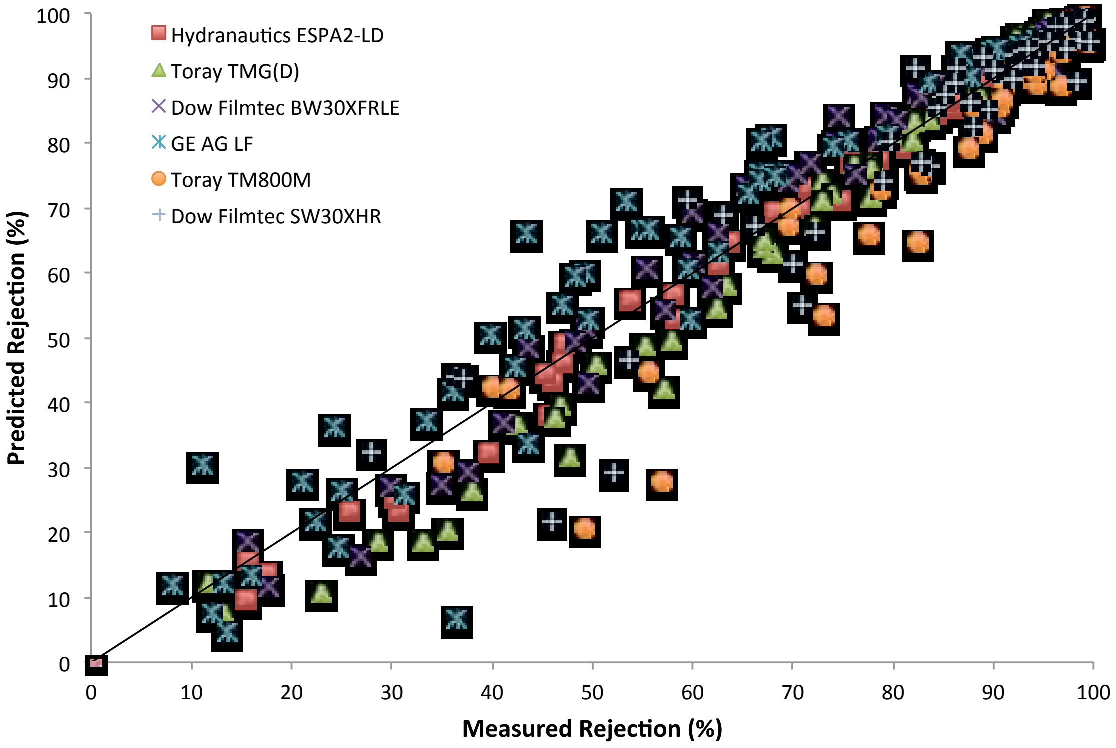
The GE AP membrane is an ultra-low pressure RO membrane. The rejection of boron through the GE AP membrane is 17%, with the next highest rejection of boron being 36% for the GE AG LF. The over prediction of the GE AP could be due to the very low rejection of boron through this membrane. Furthermore, the GE AP membrane would be restricted for use in any water reuse facility in the state of California, as the average rejection of NaCl is reported as 95% on the GE AP membrane specification sheet. The California Department of Health requires NaCl rejections of greater than 99.2% for use in water reuse facilities. For these reasons, the model did not include the GE AP membrane. This suggests that organics rejection through ultra-low pressure membranes cannot be predicted in the linear regression model presented. Figure 4.9 presents the measured versus predicted rejection by using Equation 4.8, without the GE AP membrane. The slope of the line without the GE AP membrane is 0.821.

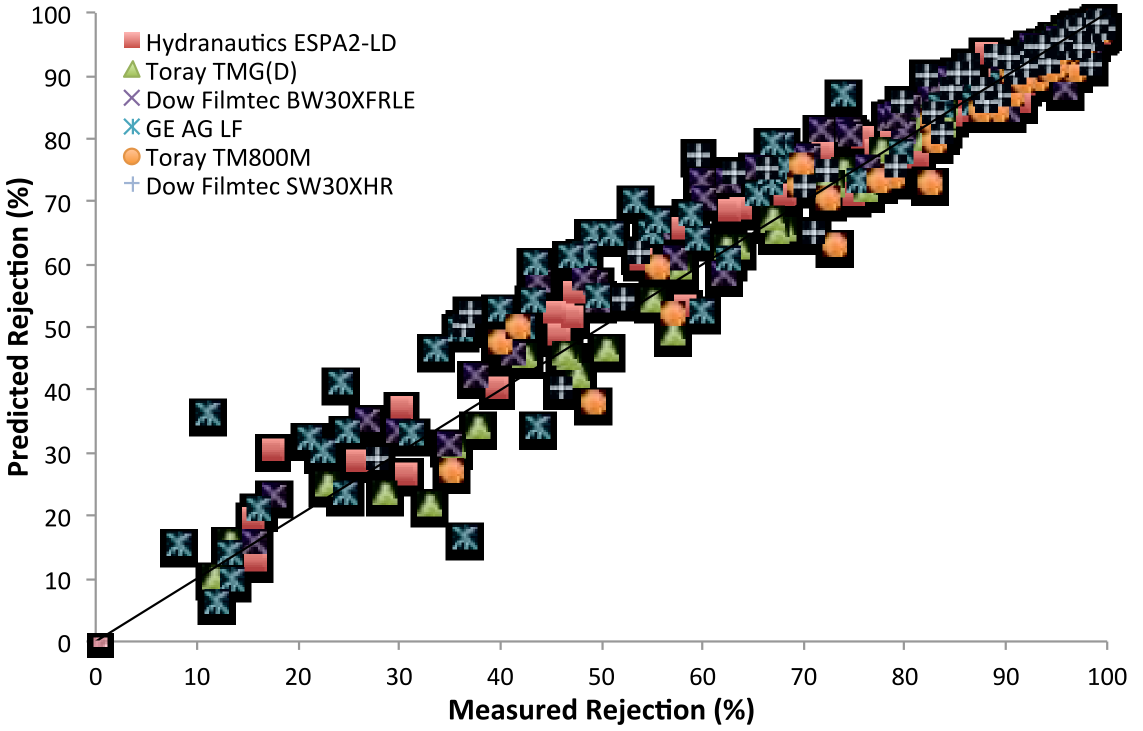
After boron was chosen as the membrane descriptor in the model, all other membranes were explored for use as the reference membrane in place of the Hydranautics ESPA2-LD. The measured versus the predicted rejections for each organic using the Toray TMG(D) as the reference membrane is seen in Figure 4.10.

The Toray TMG(D) was found to be the second best reference membrane for



[redacted]

model development, with other membranes giving poorer results for the prediction of the organics rejection. Much of the predicted organics rejection through the GE AG LF and Dow Filmtec BW30XFRLE were over predicted when using the TMG(D) as the reference membrane. However, using mass transfer coefficients for boron the seawater membranes predicted organics rejection improved with the use of the TMG(D) as the reference. However, when using this model to compare rejection by membrane products for water reuse applications, it is best to have a model that predicts performance of brackish water membranes as well. Although it could be argued that the TMG(D) membrane should be used in place as the ESPA2-LD, the ESPA2-LD's frequent use in industry makes it a good choice for the reference. The predicted rejection of organic compounds by this model must be confirmed through the reference membrane, making the widely used ESPA2-LD a good choice for the reference. The use of the Hydranautics ESPA2-LD membrane was continued through the rest of the discussion.



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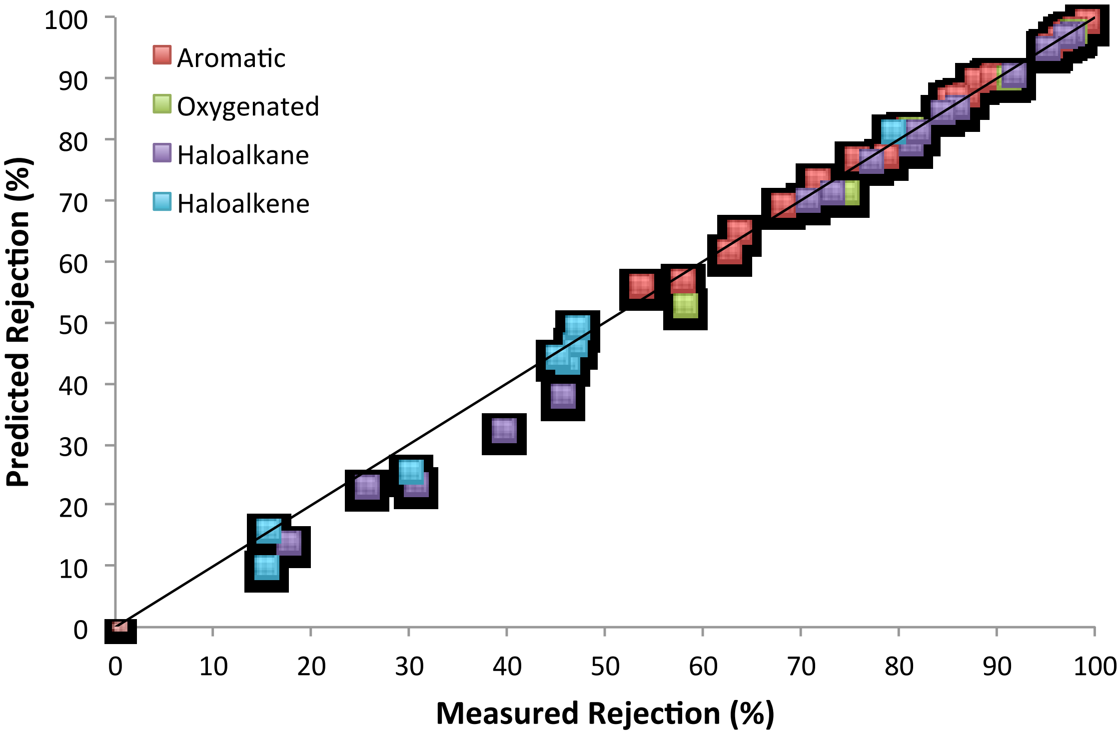
4.6 Predicted Rejection of Organics for Each Membrane

The groups of organic compounds and how they are predicted by the model is presented in Figures 4.11 to 4.16. The measured versus predicted rejections for each organic compound group by each membrane individually is presented in Figures 4.11 to 4.16. Generally, the compounds with the lowest error in the predicted rejections are the oxygenated and aromatic compounds. The compounds with the highest error of the predicted rejections are the haloalkanes and haloalkenes. The haloalkanes and haloalkenes are also the lowest rejected compounds for all membranes, as the oxygenated and aromatic compounds are rejected well by each membrane. Since the ESPA2-LD membrane was used as the reference membrane, it is also subsequently the membrane with the best predicted organic rejection. The membranes with the most error in the predicted rejection are the two seawater membranes.



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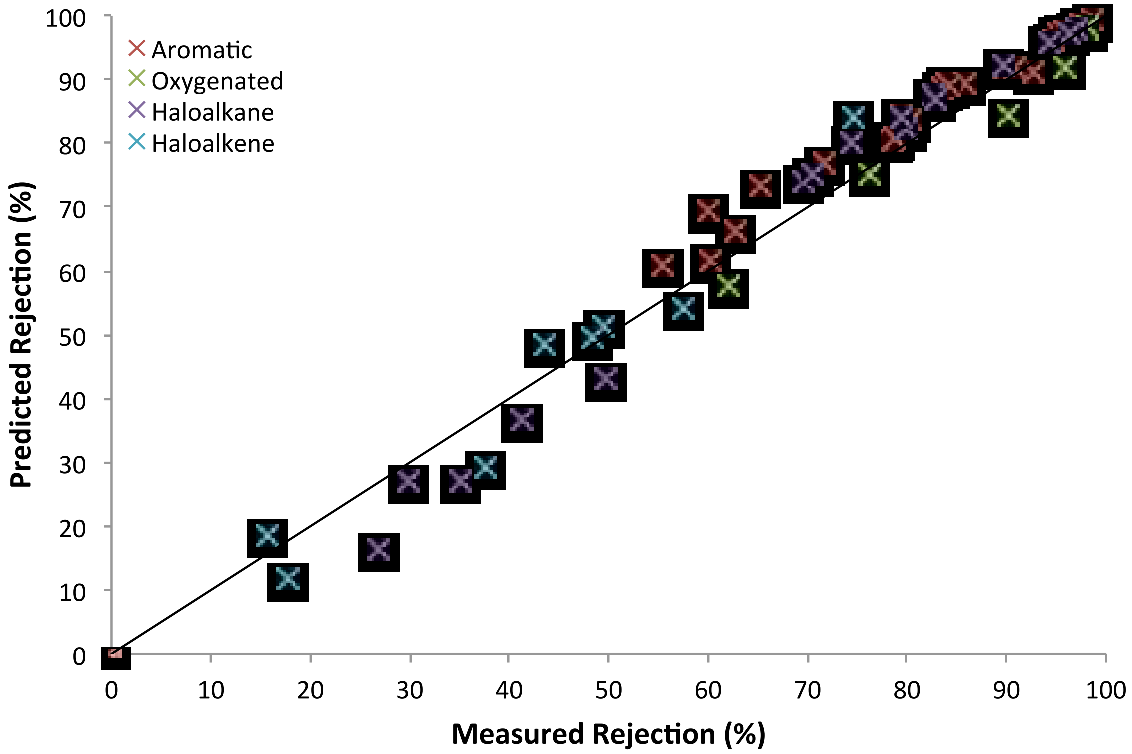

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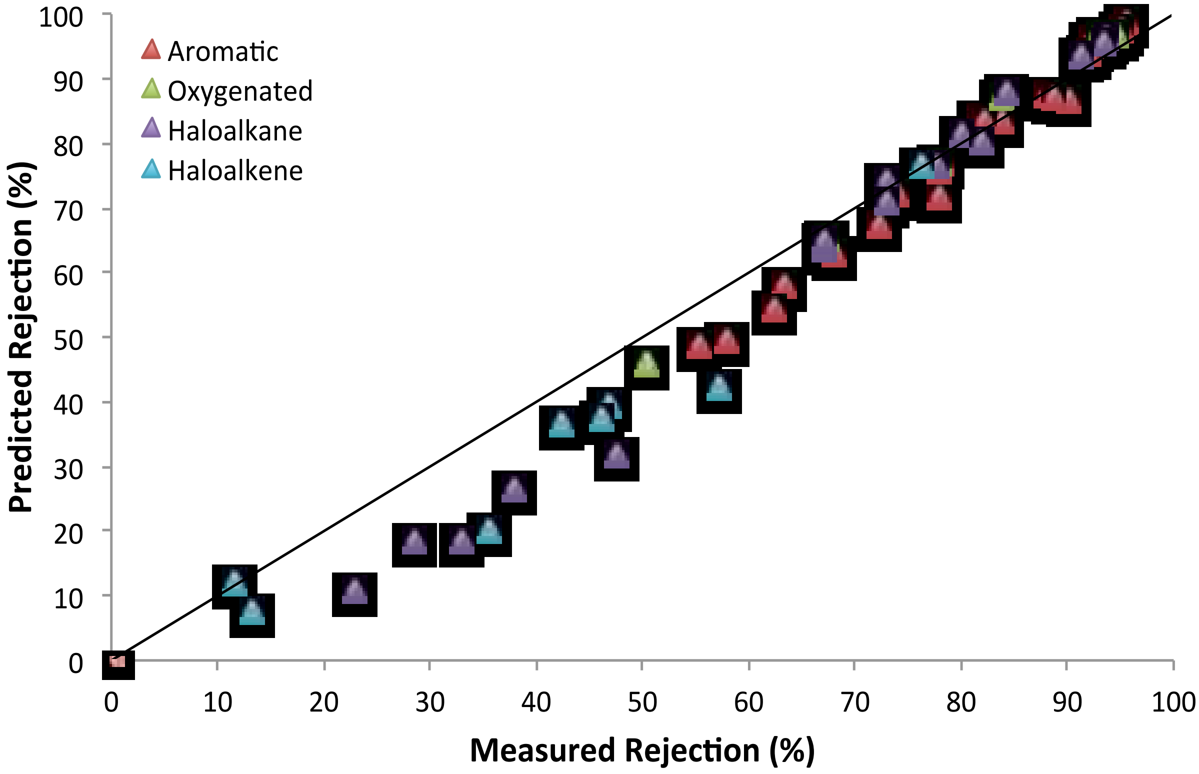

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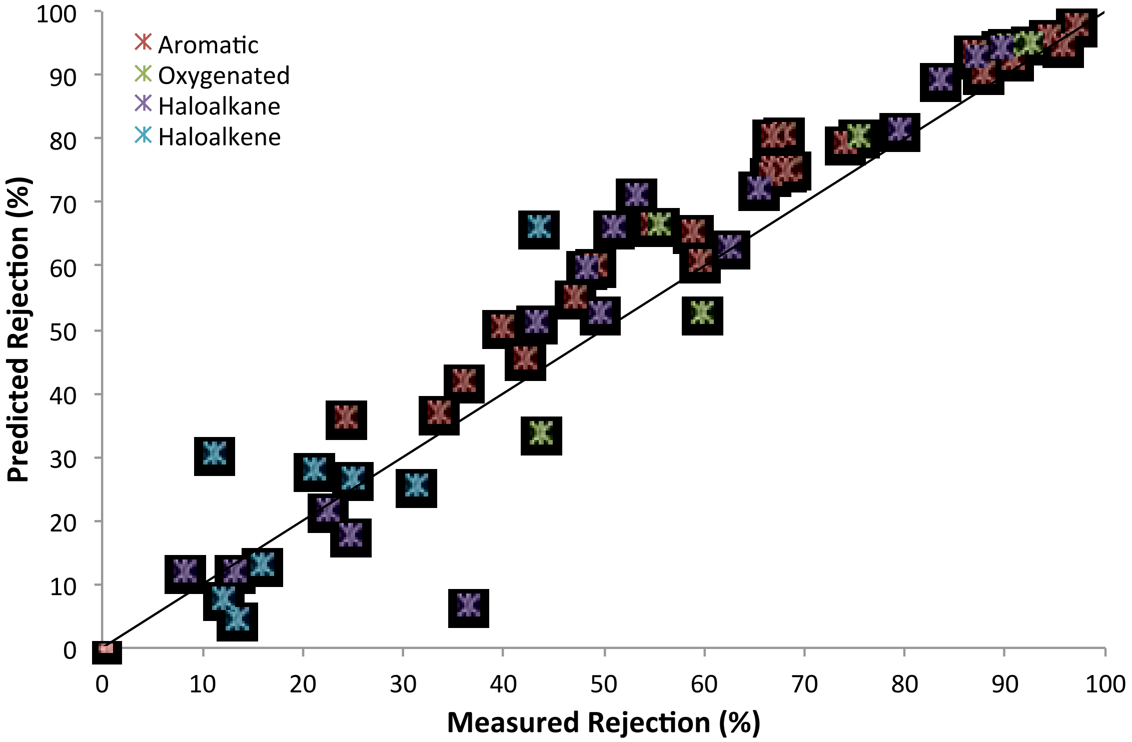

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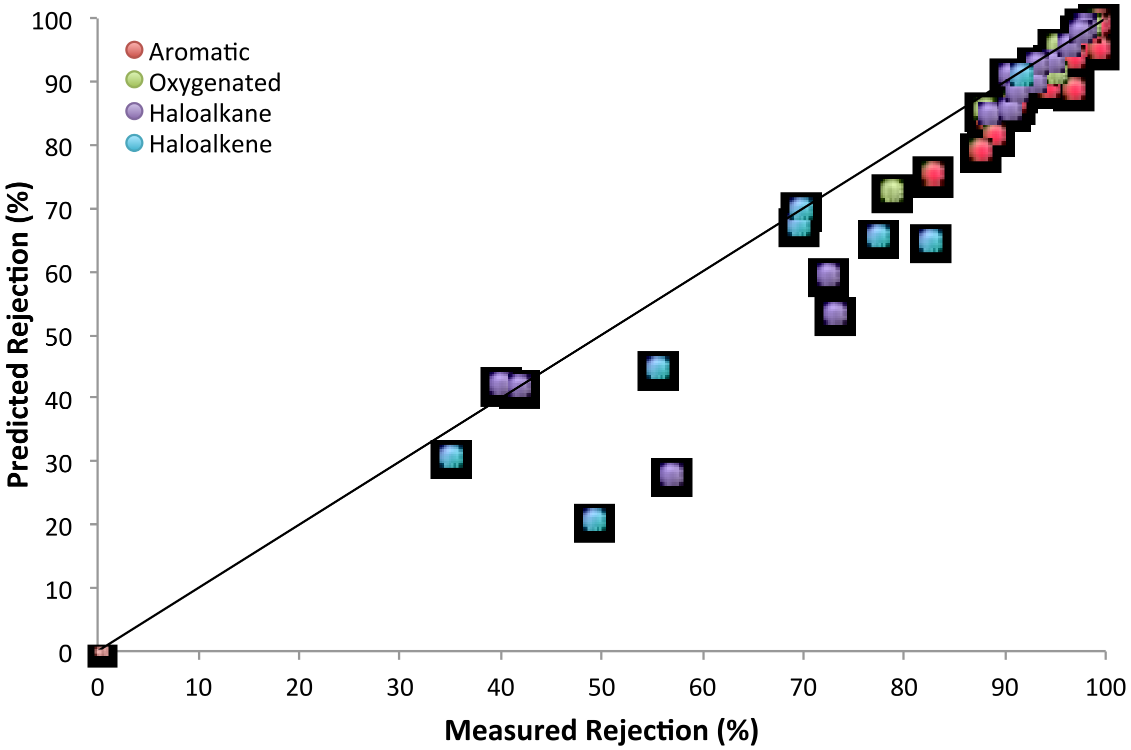

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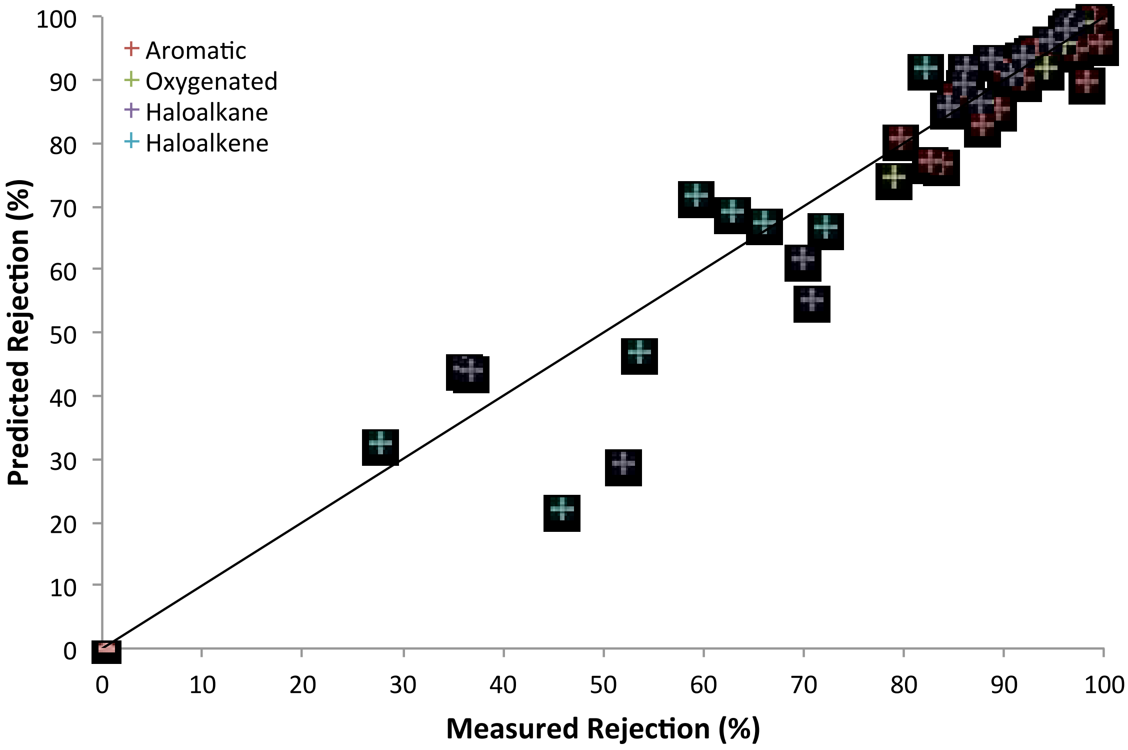

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Figures 4.11 to 4.16 present another interesting result. Between the four brackish water membranes, the GE AG LF generally had the lowest solute rejection. The three other brackish water membranes (ESPA2-LD, TMG(D), BW30XFRLE) all had very similar rejection of each organic compound. The two seawater membranes had the highest solute rejection. The aromatics and oxygenated compounds were had the highest rejection among all six membranes. Both the haloalkane and haloalkene compounds were frequently rejected below 50% by the brackish water membranes. Although the rejections of haloalkane and haloalkene compounds were slightly higher through the two seawater membranes, the rejections were still relatively low. The difference in rejection between membrane products and organic groups are due to differences in functional groups between organics, as well as difference in membrane chemistry.

4.7 Discussion and Future Work

Through the method described above, a model was created to predict rejection of low molecular weight organics by any RO membrane where the boron rejection is known. The model uses the ESPA2-LD organics and boron rejection as inputs into the linear regression model. The model was created with six different RO membranes and 54 organic compounds. The membranes represent a wide range of products for model development. The organic compounds were chosen to represent a wide range of functional chemistry. The model is possibly limited to the use of brackish and seawater membrane products, as performance of an ultra-low pressure membrane did not fit the model well.

The model created is beneficial to industry in many ways. As shown above, the water mass transfer coefficient and sodium chloride rejection of membrane products are not useful when comparing different membranes for their organics rejection. Therefore, the use of the k_W and NaCl rejection are not practical to understanding organics rejection through many different RO membranes. The model allows comparison of membrane performance for a wide range of compounds based on rejection of boron, a commonly reported parameter, instead of having to conduct expensive and difficult testing for each compound.

This model could be used to measure the age or possible damage of membrane material. More research would need to be completed, as the experiments conducted for model development did not include experiments with aged membranes. More generally, however, if operators notice a decrease in boron rejection, they can also assume that a decrease in organics rejection is also occurring.

Validating the generated model can be done by testing different organic compounds on the membrane products used in this study. This would provide a dataset outside of the one used for model development to be used to test and validate the model. Future studies involving aged membranes could also be completed, as discussed above. This would allow for a more complete understanding of how boron can be used to predict organics rejection through reverse osmosis membranes.

5. Conclusion

Bench-scale RO experiments were completed using 8 different membrane products and 73 organic compounds. The membrane products consisted of nanofiltration, ultra-low pressure, brackish water, and seawater membranes. The organic chemicals in the study were chosen to investigate the removal of neutral, low molecular weight compounds. The rejection of NaCl, boron, and each of the organic compounds were measured in each experiment.

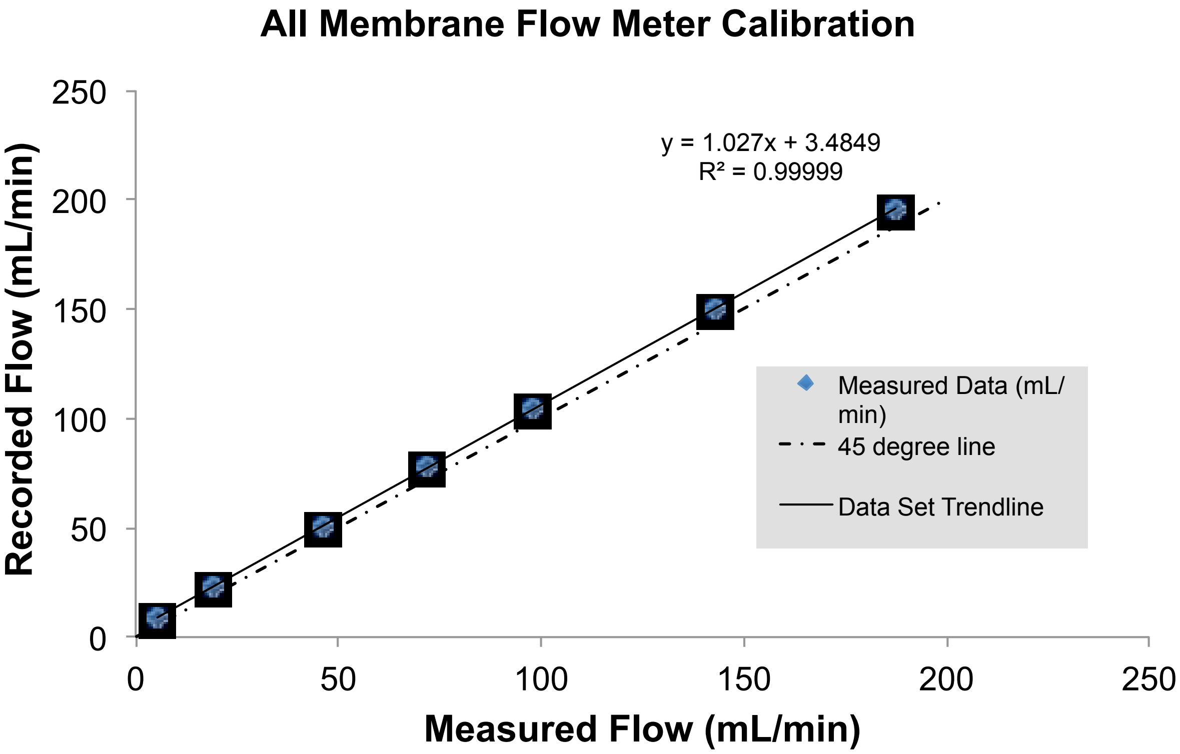
The rejection of the organic compounds through the Hydranautics ESPA2-LD membrane were compared to each other. The industry accepted guidelines that govern rejection of organic compounds were supported in some instances, but many other trends were observed in the comparison of the organic compounds rejection to each other. The structure and functional chemistry of organic compounds is important to consider when investigating rejection of these compounds through RO membranes.

A linear regression model was then created to predict the organics rejection through the varying membrane products tested. The boron mass transfer coefficient was utilized as the reference between membranes because it is already being placed by membrane manufacturers on many seawater membrane specification sheets. The linear regression model will be useful to the water reuse industry by allowing a non-volatile and easily measured compound to serve as a reference for organics rejection through the membranes chosen for use in water reuse facilities.

Section 1: Calibration of the 0-200 mL/min Permeate Flow Meter

Make/Model: Cole-Parmer Instrument Company/32908-45
SN: 133974
Specified Accuracy: ±2% of Full Scale
Date of Calibration by UNM: August 16, 2016

This flow meter is used to measure the combined permeate flow from all 5 membrane cells. The flow meter was wired to the data acquisition system, which was collecting data continuously every five seconds though the entire calibration time. Deionized water was pumped through the experimental setup and the flow meter by a Cole-Parmer Digital Gear Pump. The flow on the gear pump was adjusted until the desired calibration flow rates were reached. At the 8 desired flow rates used to create the calibration curve, water was collected into a plastic container and weighed. The scale used to determine the weight was a Mettler Toledo (model PB3002-S) that was capable of reading to the nearest 0.01 gram. The scale was zeroed at the beginning of each of the times the water was collected. Using a stopwatch that measured to the nearest 0.01 second, the time it took for the weighed amount of water to collect in the plastic container was recorded. It was attempted to collect water for at least a minute in order to improve the accuracy of the measurements. The weight of the water divided by the time it took to collect the water is the measured flow value at that calibration point. The flow data collected by the data acquisition system during the time water was collecting into the plastic container was averaged and used as the recorded flow value. The measured flow and the recorded flow were compared, as can be seen in Figure 1.1.



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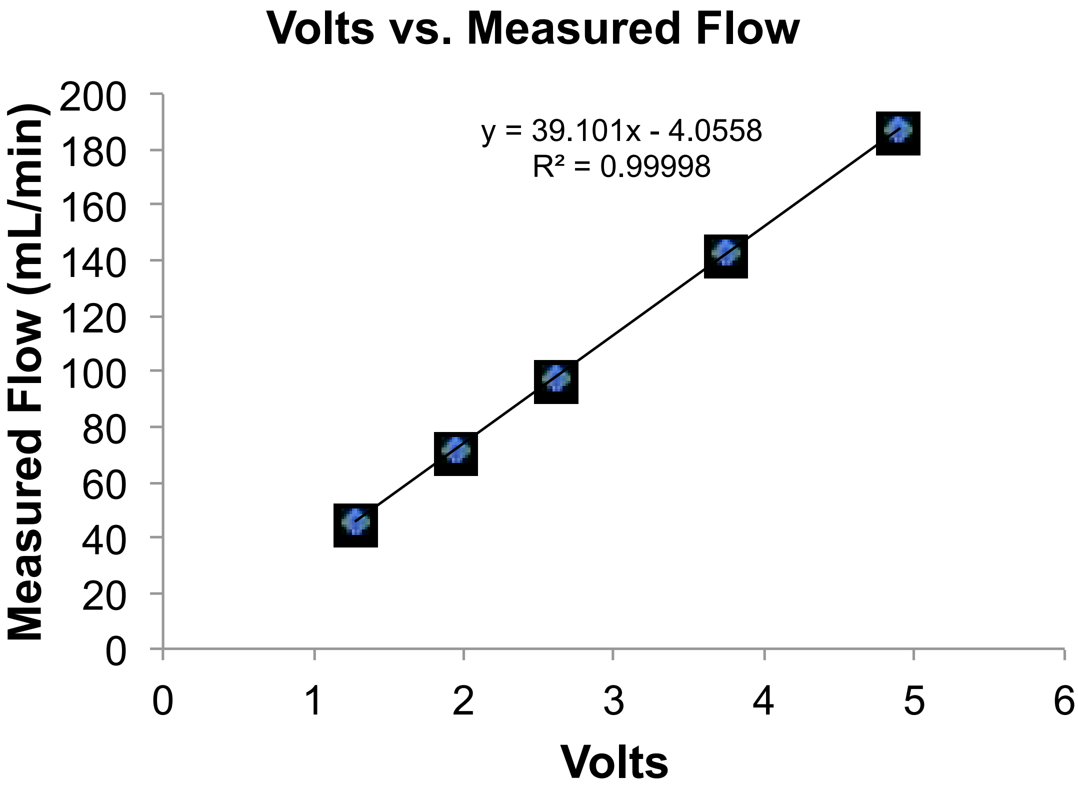
Volts	Flow (mL/min)
0	0
5	200

Table 1.1: Initial parameters in data acquisition system.



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Using the parameter values originally input into the data acquisition system, seen in Table 1.1, a linear equation was constructed relating the voltage and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 1.2 shows this relationship.

Using the trendline equation in Figure 1.2, new parameter input values were obtained by plugging in 0 volts and 5 volts into the equation. The new parameters can be seen in Table 1.2.

Table 1.2: Parameters entered into data acquisition system after calibration

Volts	Flow (mL/min)
0	-4.0558
5	191.4492

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration.

Figure 1.3 below shows this calibration check. Table 1.3 shows the accuracy of the measurements at the various calibration points after the new parameters were entered in the data acquisition system. The measured accuracy was significantly better than the specified accuracy of the instrument. The measured accuracy is sufficient to record the permeate flow to within 1 mL/min over nearly whole range, which is sufficient to determine permeate flux measurements to within 1 L/m^2-h over the entire range.

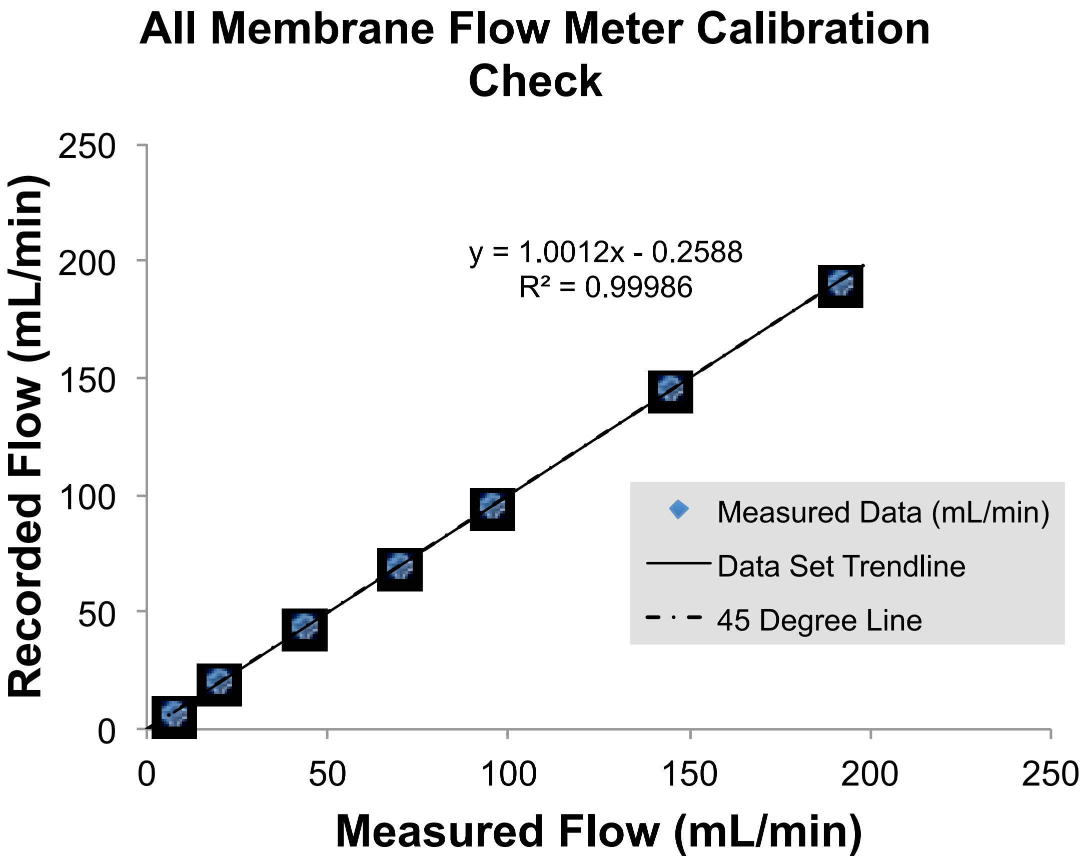

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Table 1.3: Accuracy of measurements after calibration of flow meter

Measured Flow (mL/min)	Recorded Flow (mL/min)	Error (% of full scale)
7.45	6.18	0.64
20.23	20.16	0.04
43.76	44.35	0.30
70.04	69.80	0.12
95.86	95.72	0.07
144.83	145.81	0.49
191.82	190.86	0.48

Section 2: Calibration of the 0-50 mL/min Permeate Flow Meter

Make/Model: Cole-Parmer Instrument Company/32908-43
SN: 128306
Specified Accuracy: ±2% of Full Scale
Date of Calibration by UNM: August 16, 2016

This flow meter is used to measure the permeate flow from an individual membrane cell. The calibration approach was identical to that in Section 1, although the calibration data was collected at 7 flow values instead of 8. The measured flow and the recorded flow were compared, as can be seen in Figure 2.1.

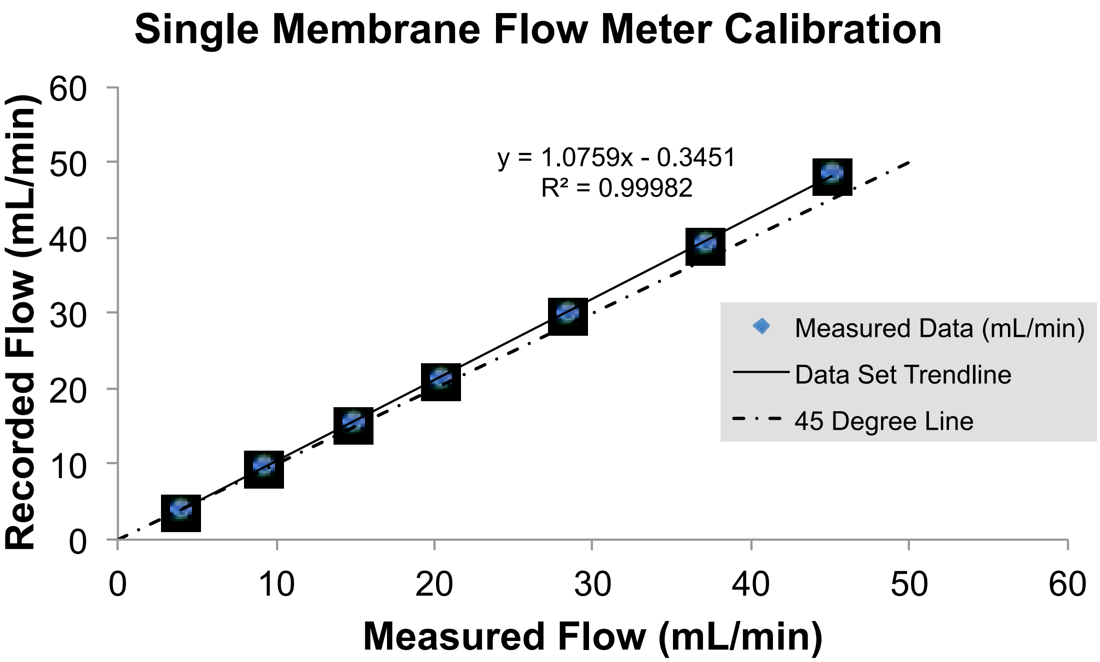

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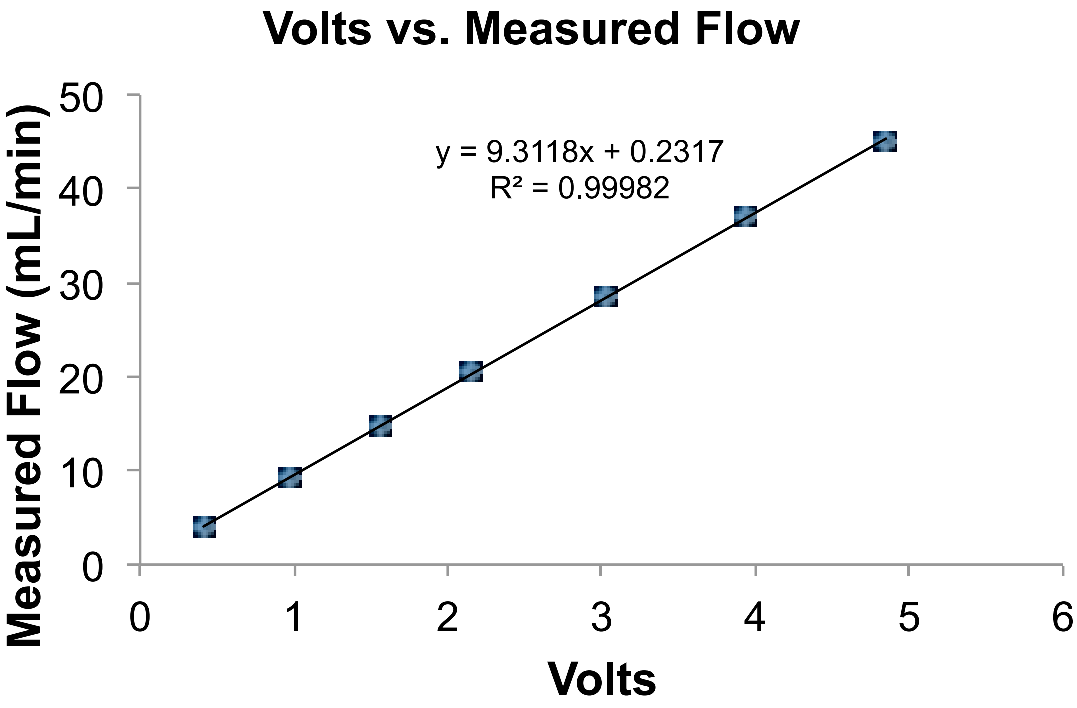
Table 2.1: Initial parameters in data acquisition system

Volts	Flow (mL/min)
0	0
5	50

Using the parameter values originally input into the data acquisition system, seen in Table 2.1, a linear equation could be constructed relating the volts and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 2.2 shows this relationship.



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Using the trendline equation in Figure 2.2, new parameter input values were obtained by plugging in 0 volts and 5 volts into the equation. The new parameters can be seen in Table 2.2.

Table 2.2: Parameters entered into data acquisition system after calibration

Volts	Flow (mL/min)
0	0.2317
5	46.7907

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration. Figure 2.3 below shows this calibration check. Table 2.3 shows the accuracy of the measurements at the various calibration points after the new parameters were entered in the data acquisition system. The measured accuracy was significantly better than the specified accuracy of the instrument. The measured accuracy is sufficient to record the permeate flow to within 0.25 mL/min over the entire range, which is sufficient to determine permeate flux measurements to within 0.9 L/m^2-h over the entire range.

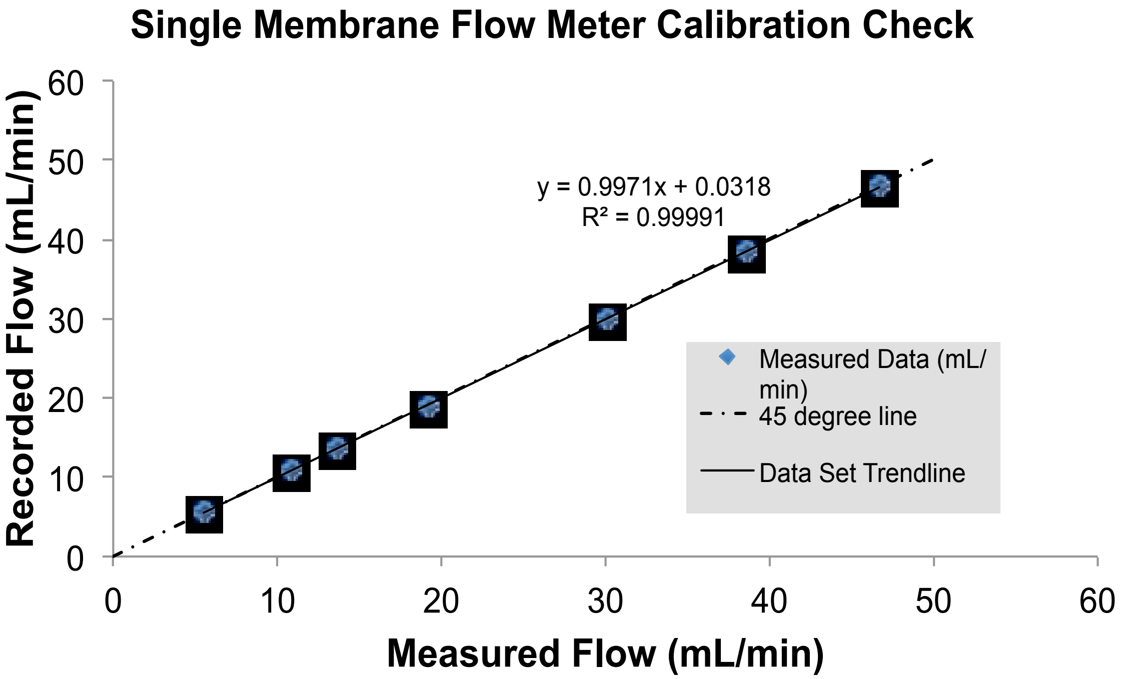

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Table 2.3: Accuracy of measurements after calibration of flow meter

Measured Flow (mL/min)	**Recorded Flow (mL/min)**	**Error (% of full scale)**
5.51	5.68	0.34
10.90	10.96	0.12
13.70	13.68	0.04
19.22	19.01	0.42
30.09	29.86	0.46
38.59	38.47	0.24
46.69	46.77	0.16

Section 3: Calibration of the 0.1-1 L/min Concentrate Flow Meter

Make/Model: McMillan Flow/104-6
SN: 3658
Specified Accuracy: + 0.6%/-1% of Full Scale
Date of Calibration by UNM: August 25, 2016

This flow meter is used to measure the concentrate flow after the last membrane cell. The calibration approach was identical to that in Section 1, although the calibration data was collected at 6 flow values instead of 8. The measured flow and the recorded flow were compared, as can be seen in Figure 3.1.

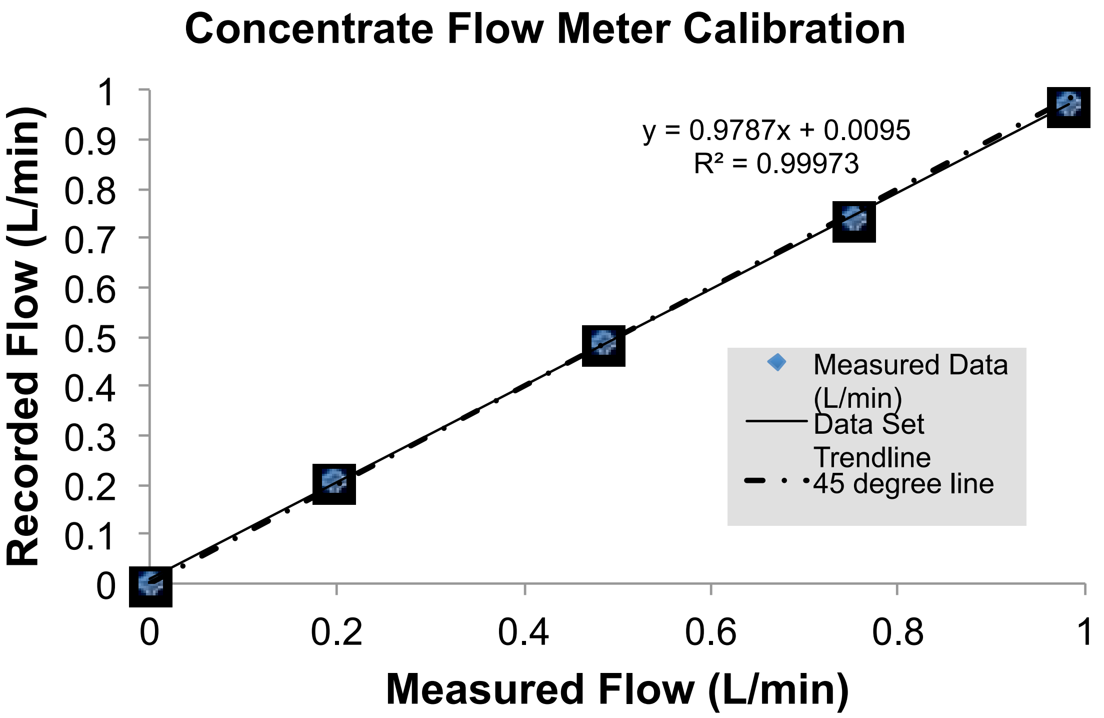

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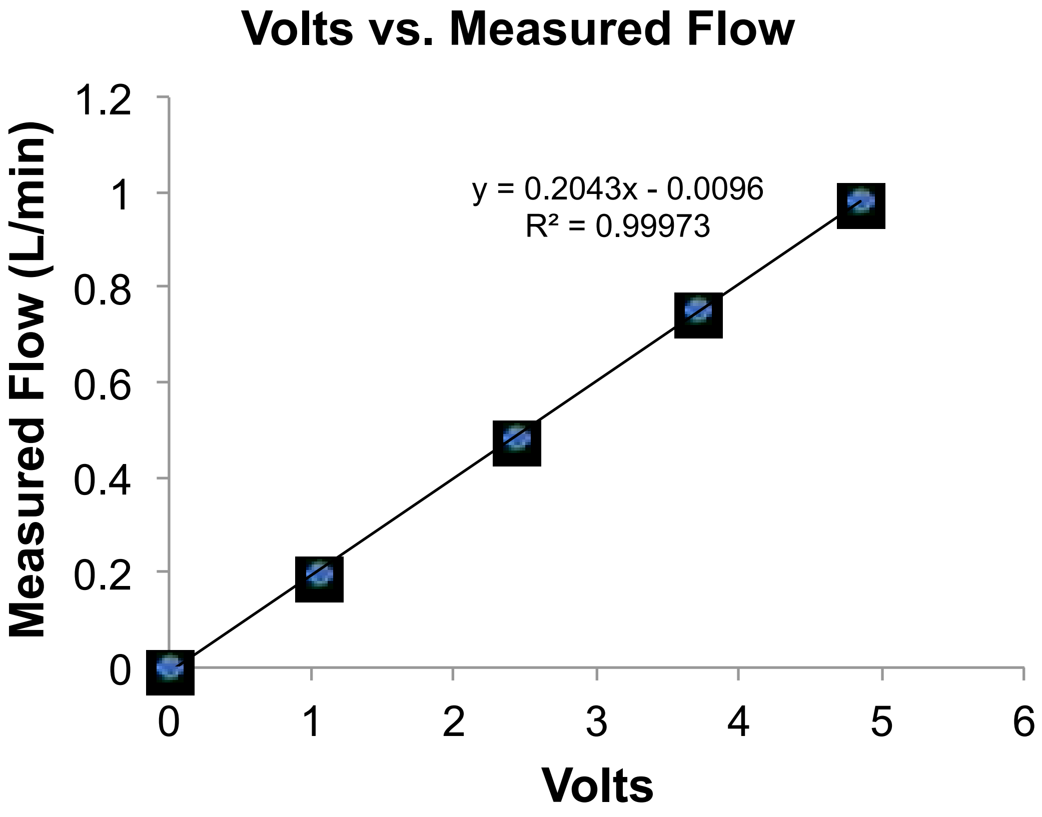
Table 3.1: Initial parameters in data acquisition system

Volts	Flow (L/min)
0	0
5	1

Using the parameter values originally input into the data acquisition system, seen in Table 3.1, a linear equation could be constructed relating the volts and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 3.2 shows this relationship.



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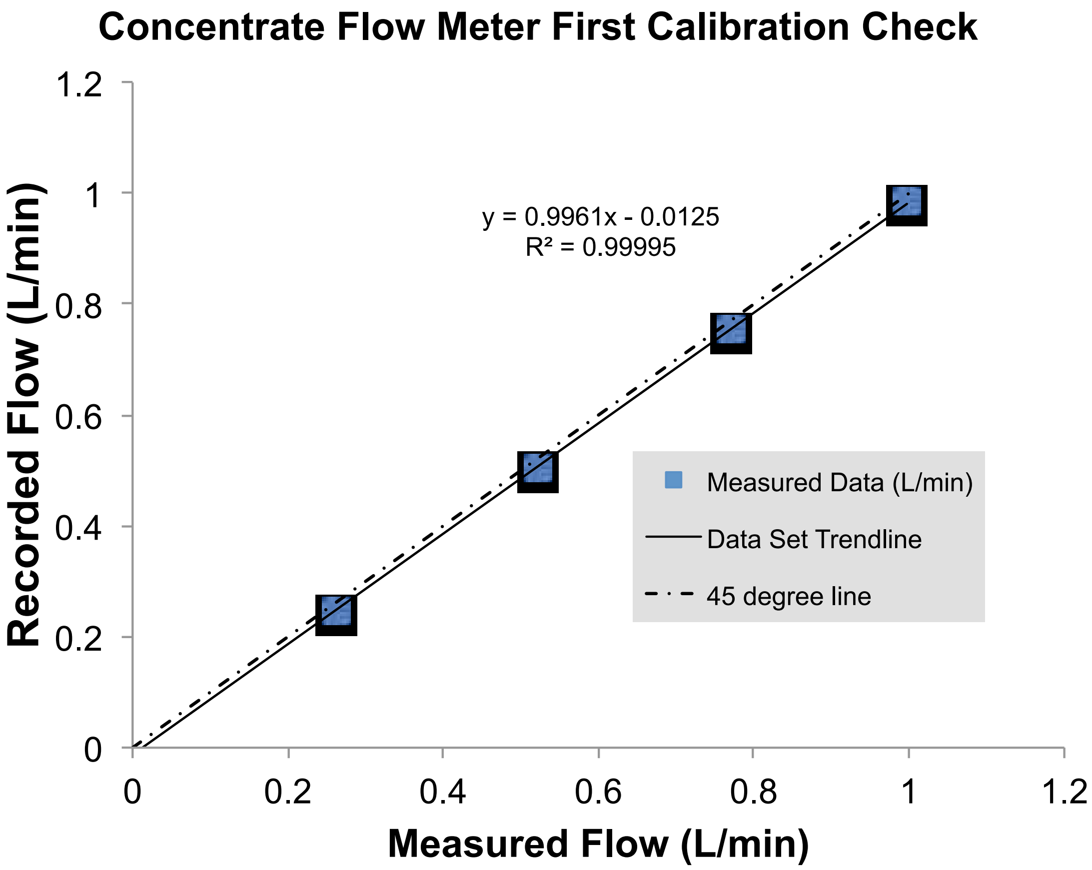
Using the trendline equation in Figure 3.2, new parameter input values were obtained by plugging in 0 volts and 5 volts into the equation. The new parameters can be seen in Table 3.2.

Table 3.2: Parameters entered into data acquisition system after calibration

Volts	Flow (L/min)
0	-0.0096
5	1.0119

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration. Figure 3.3 below shows this calibration check.



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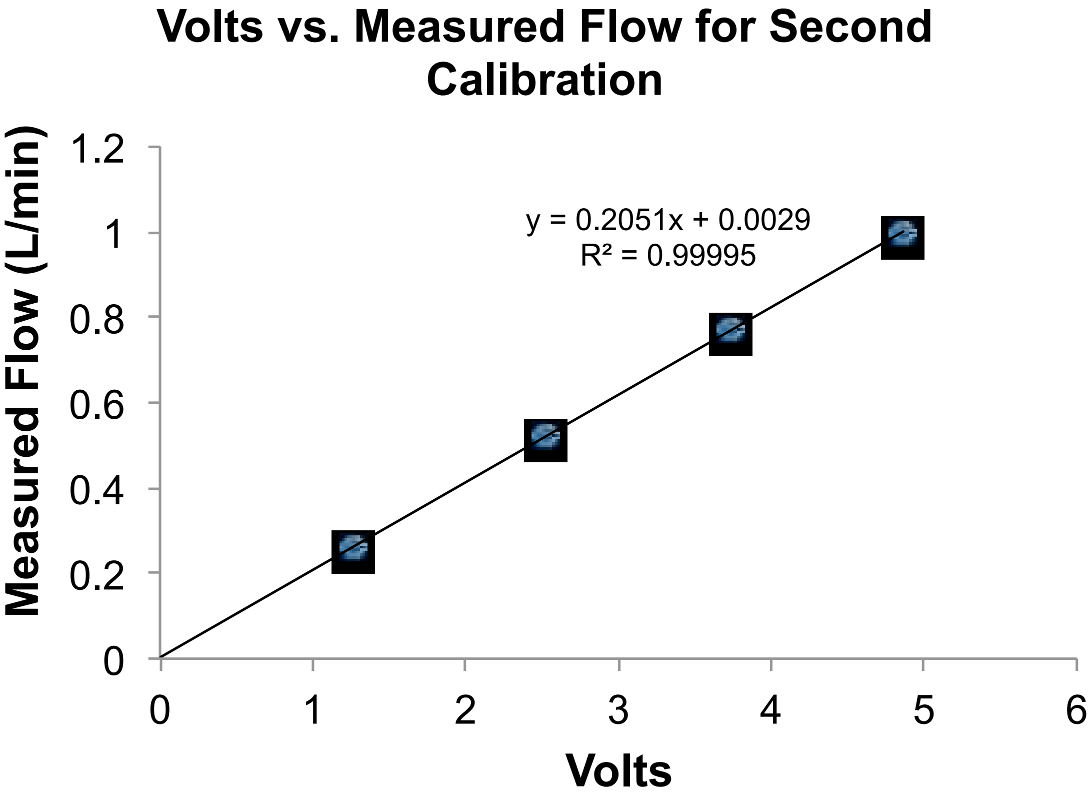
It can be seen that even with the entered parameters in Table 3.2, the instrument is still not sufficiently calibrated. A second iteration of the calibration process was completed, using the same method described in Section 1 with 6 flow values. Using the parameters input into the data acquisition system, Table 3.2, a linear equation could be constructed again relating the volts and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 3.4 shows this relationship.



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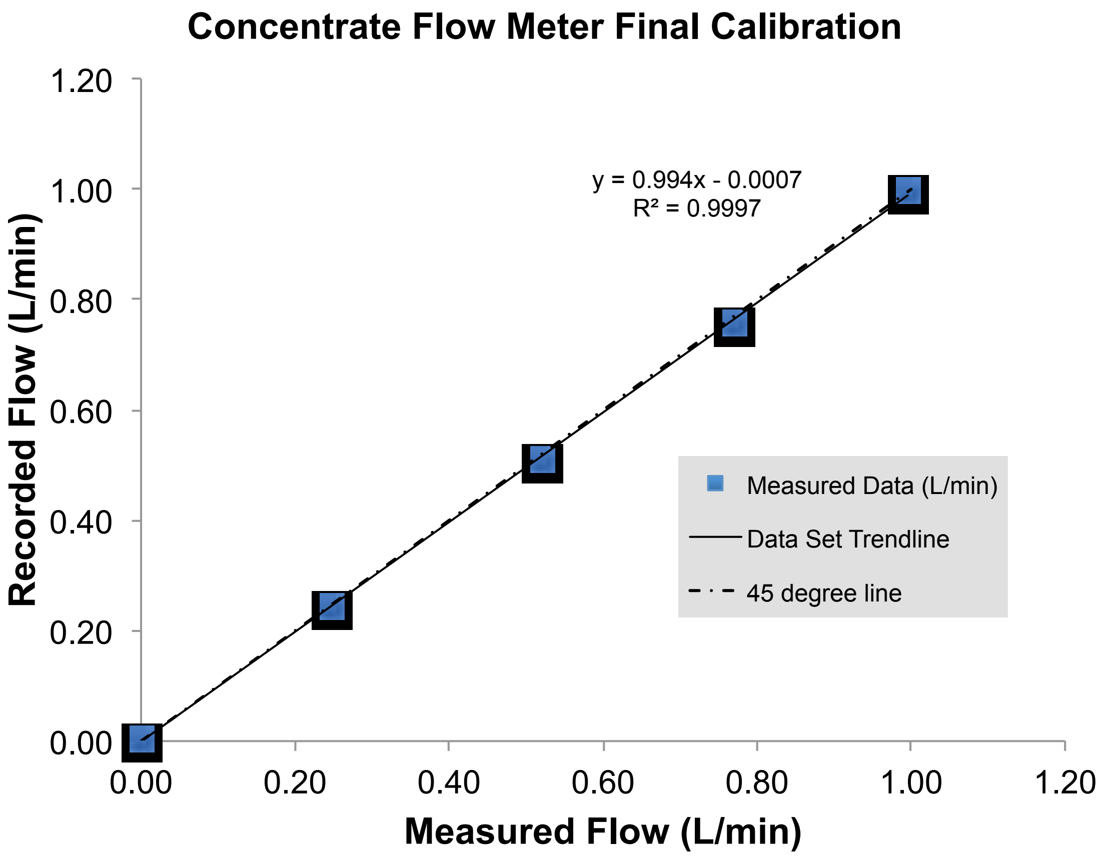
Using the trendline equation in Figure 3.4, new parameter input values were obtained by plugging in 0 volts and 5 volts into the equation. The new parameters can be seen in Table 3.3.

Table 3.3: Parameters entered into data acquisition system after calibration

Volts	Flow (L/min)
0	0.0029
5	1.0284

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration. Figure 3.5 below shows this calibration check. Table 3.4 shows the accuracy of the measurements at the various calibration points after the new parameters were entered in the data acquisition system. The measured accuracy was significantly better than the specified accuracy of the instrument. The measured accuracy is sufficient to record the permeate flow to within 0.01 L/min over the entire range, which is sufficient to determine concentrate flux measurements to within 0.04 L/m^2-h over the entire range.



[redacted]

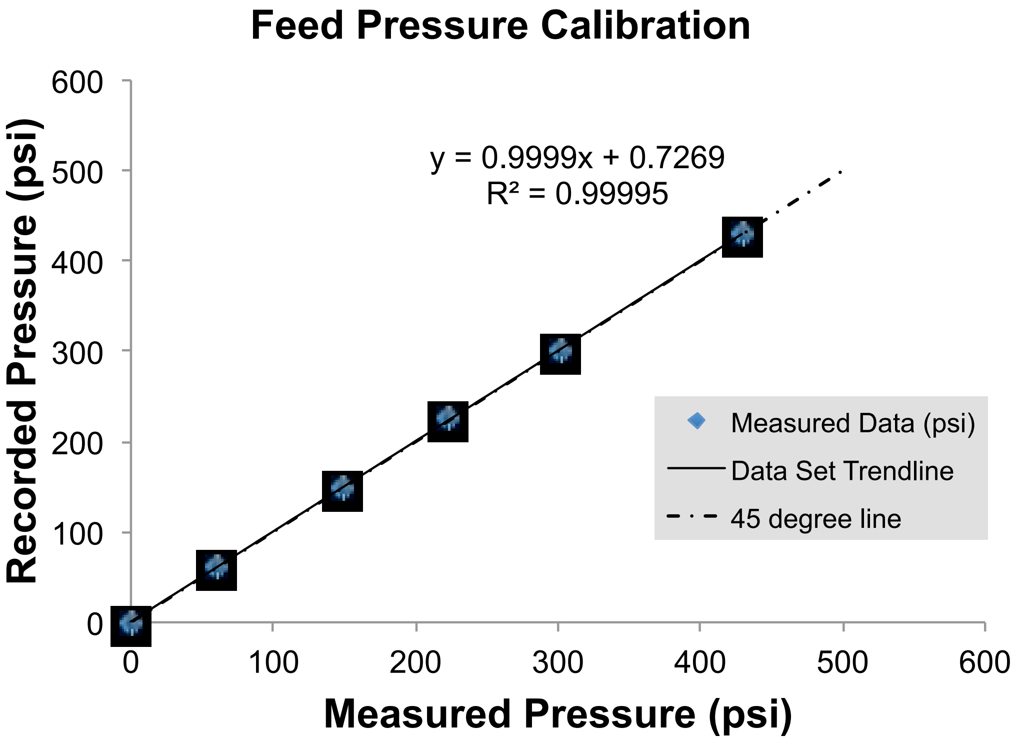
Table 3.4: Accuracy of measurements after calibration of flow meter

Measured Flow (L/min)	Recorded Flow (L/min)	Error (% of full scale)
0	0.00	0.00
0.25	0.25	0.00
0.52	0.51	0.00
0.77	0.76	0.00
1.00	1.00	0.00

Section 4: Calibration of the 0-500 psi Feed Pressure Transducer

Make/Model: Cole-Parmer/ C206
SN: 6911831
Specified Accuracy: ±0.13% of Full Scale
Date of Calibration by UNM: August 15, 2016

This pressure transducer is used to measure the feed pressure entering into the membrane cells. The pressure transducer was wired to the data acquisition system, which was collecting data continuously every five seconds through the entire calibration time. Deionized water was pumped through the experimental setup and the pressure transducer by a Wanner Hydra-Cell D03 positive displacement pump with variable speed drive. A WIKA calibrated test gage was used. At the 6 desired pressures used to create the calibration curve, readings were read from the calibrated pressure gage and used as the measured feed pressure values. The pressure data collected by the data acquisition system during the time the pressure measurements were being read from the calibrated pressure gage was averaged and used as the recorded pressure value. The measured pressure and recorded pressure were compared, as can be seen in Figure 4.1.

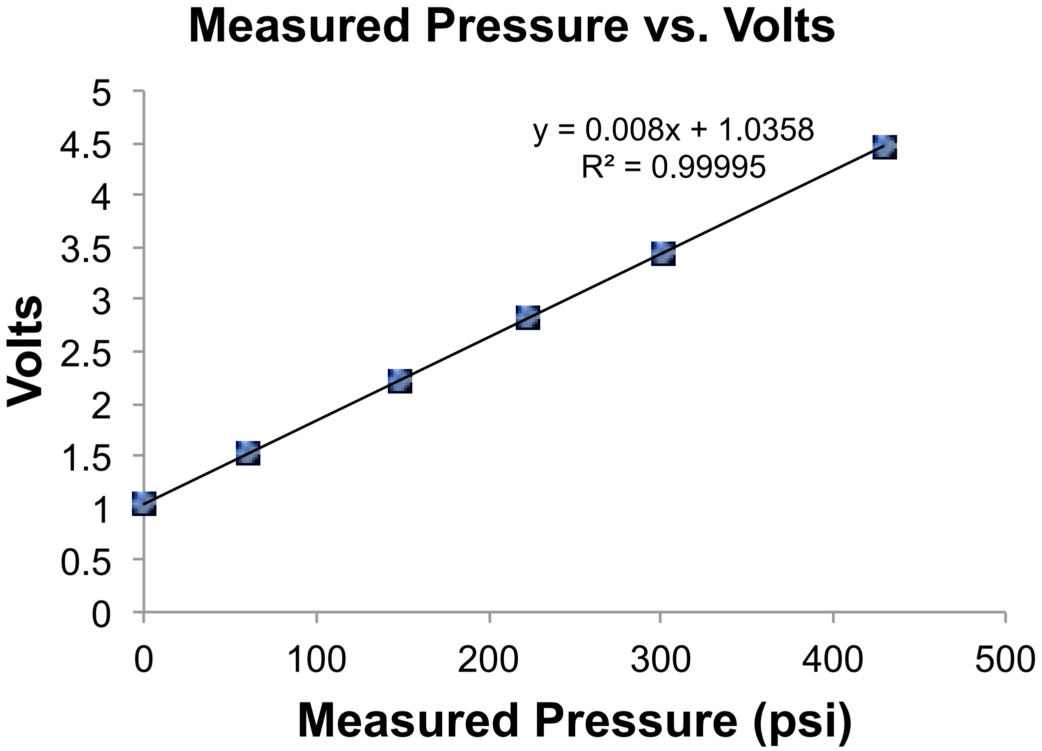


[redacted]

Table 4.1: Initial parameters in data acquisition system

Volts	Pressure (psi)
1.03	0
5.03	500

Using the parameter values originally input into the data acquisition system, seen in Table 4.1, a linear equation was constructed relating the voltage and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 4.2 shows this relationship.



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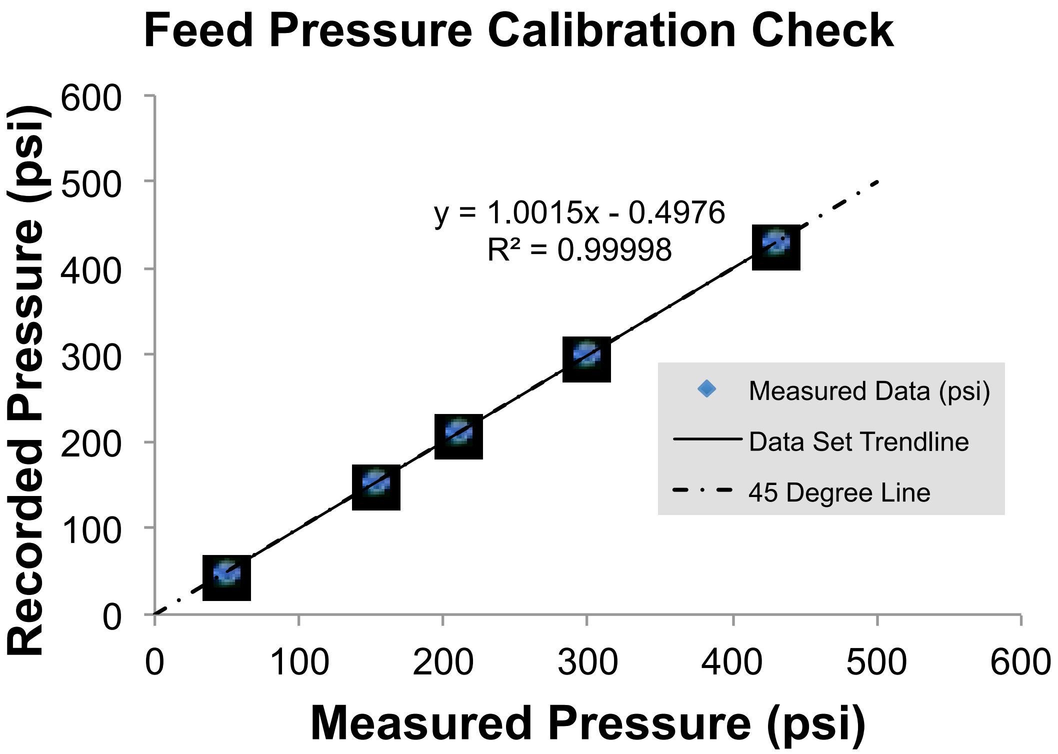
Using the trendline equation in Figure 4.2, new parameter input values were obtained by plugging in 0 psi and 500 psi into the equation. The new parameters can be seen in Table 4.2.

Table 4.2: Parameters entered into data acquisition system after calibration

Volts	Pressure (psi)
1.0358	0
5.0353	500

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration. Figure 4.3 below shows this calibration check. Table 4.3 shows the error of the measurements at the various calibration points after the new parameters were entered in the data acquisition system. The calculated error was significantly better than the specified error of the instrument. The measured error is sufficient to record the feed pressure to within 0.97 psi over the entire range.



[redacted]

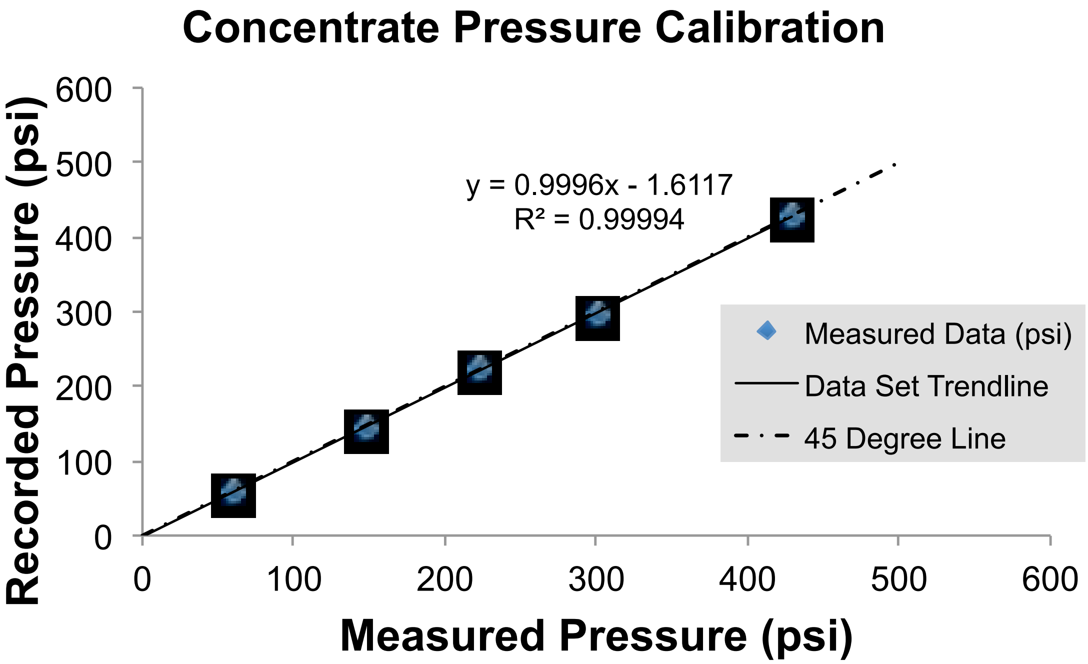
Table 4.3: Accuracy of measurements after calibration of feed pressure transducer

Measured Pressure (psi)	Recorded Pressure (psi)	Error (% of full scale)
50	49.03	-0.19
153	152.94	-0.01
211	211.78	0.16
300	299.50	-0.10
429.5	429.49	0.00

Section 5: Calibration of the 0-500 psi Concentrate Pressure Transducer

Make/Model: Cole-Parmer/ C206
SN: 2559712
Specified Accuracy: ±0.13% of Full Scale
Date of Calibration by UNM: August 15, 2016

This pressure transducer is used to measure the concentrate pressure exiting the membrane cells. The calibration methods are identical to that in Section 4. The measured pressure and recorded pressure were compared, as can be seen in Figure 5.1.



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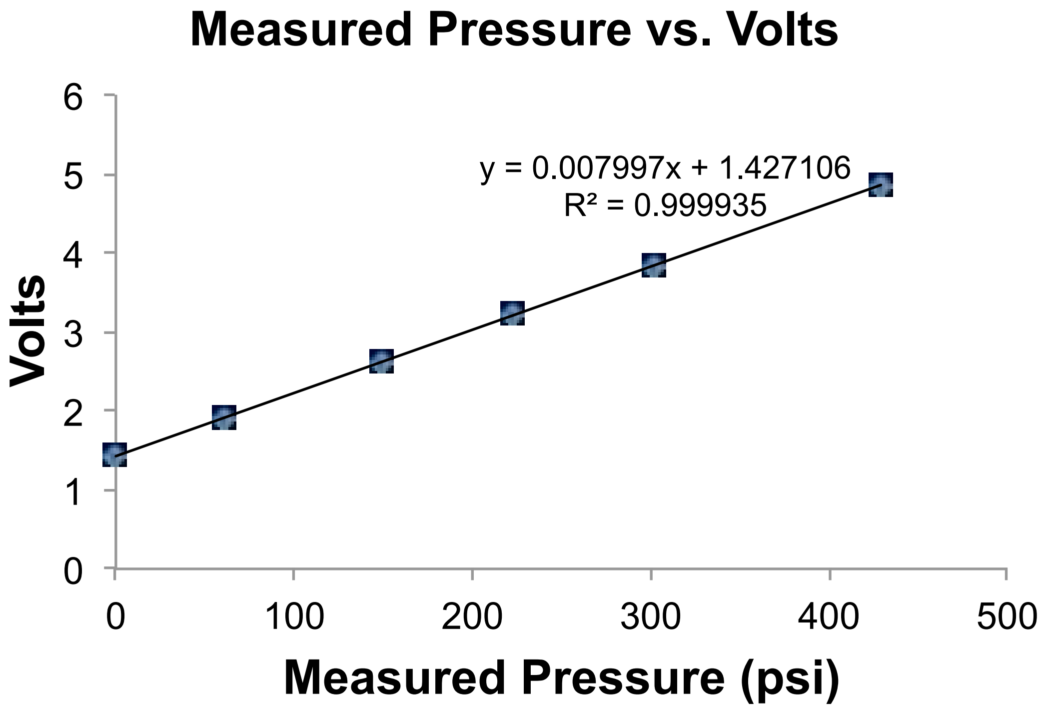
Using the parameter values originally input into the data acquisition system, seen in Table 5.1, a linear equation was constructed relating the voltage and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 5.2 shows this relationship.

Table 5.1: Initial parameters in data acquisition system

Volts	Pressure (psi)
1.44	0
5.44	500



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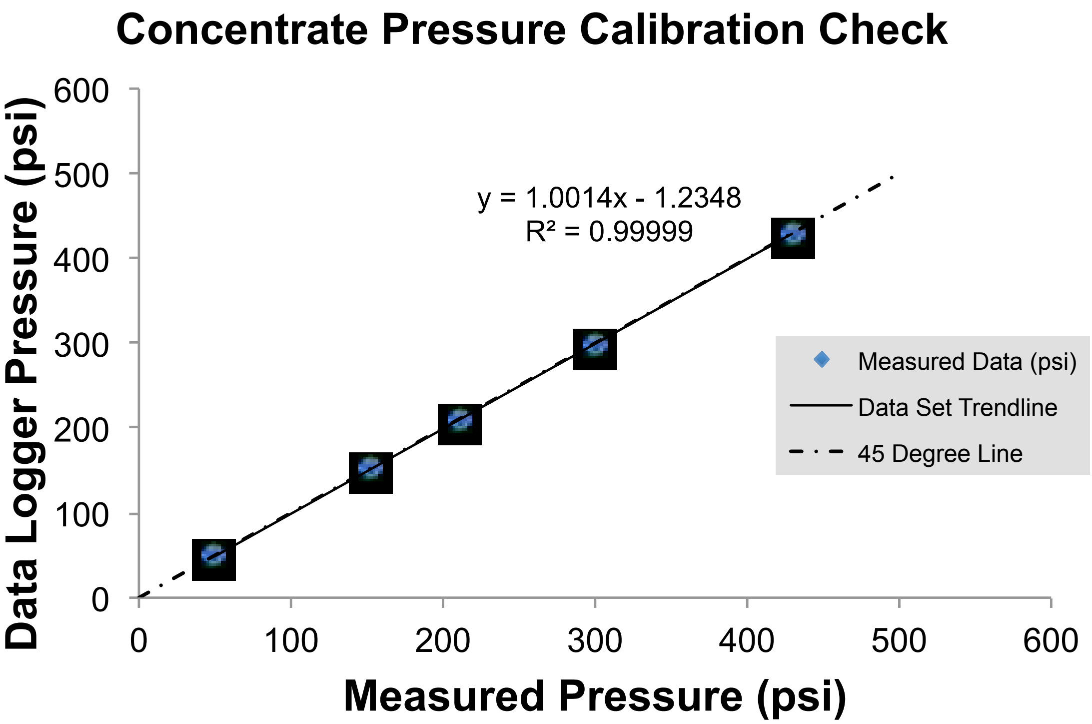
Using the trendline equation in Figure 5.2, new parameter input values were obtained by plugging in 0 psi and 500 psi into the equation. The new parameters can be seen in Table 5.2.

Table 5.2: Parameters entered into data acquisition system after calibration

Volts	Pressure (psi)
1.4271	0
5.4256	500

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration. Figure 5.3 below shows this calibration check. Table 5.3 shows the error of the measurements at the various calibration points after the new parameters were entered in the data acquisition system. The calculated error was significantly better than the specified error of the instrument. The measured error is sufficient to record the concentrate pressure to within 1.66 psi over the entire range.



[redacted]

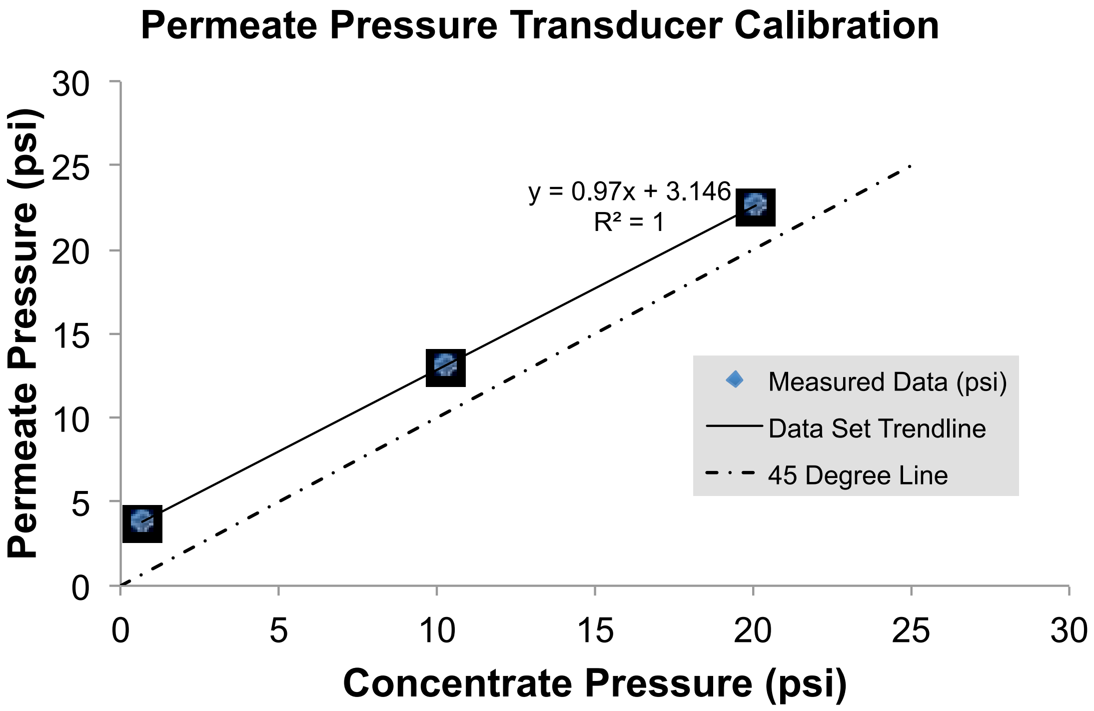
Table 5.3: Accuracy of measurements after calibration of concentrate pressure transducer

Measured Pressure (psi)	Recorded Pressure (psi)	Error (% of full scale)
50	48.89	-0.22
153	151.91	-0.22
211	210.59	-0.08
300	298.34	-0.33
429.5	429.25	-0.05

Section 6: Calibration of the 0-25 psi Permeate Pressure Transducer

Make/Model: Cole-Parmer/ C206
SN: 2582071
Specified Accuracy: ±0.13% of Full Scale
Date of Calibration by UNM: August 15, 2016

This pressure transducer is used to measure the concentrate pressure exiting the membrane cells. The permeate pressure transducer was calibrated against the concentrate pressure transduce because the WIKA calibrated test gage used for the other pressure transducer calibrations did not have a sufficient rage to provide accurate enough readings. The measured pressure in this calibration is the concentrate pressure transducer readings. These were compared to the recorded pressure of the permeate pressure transducer, as can be seen in Figure 6.1.

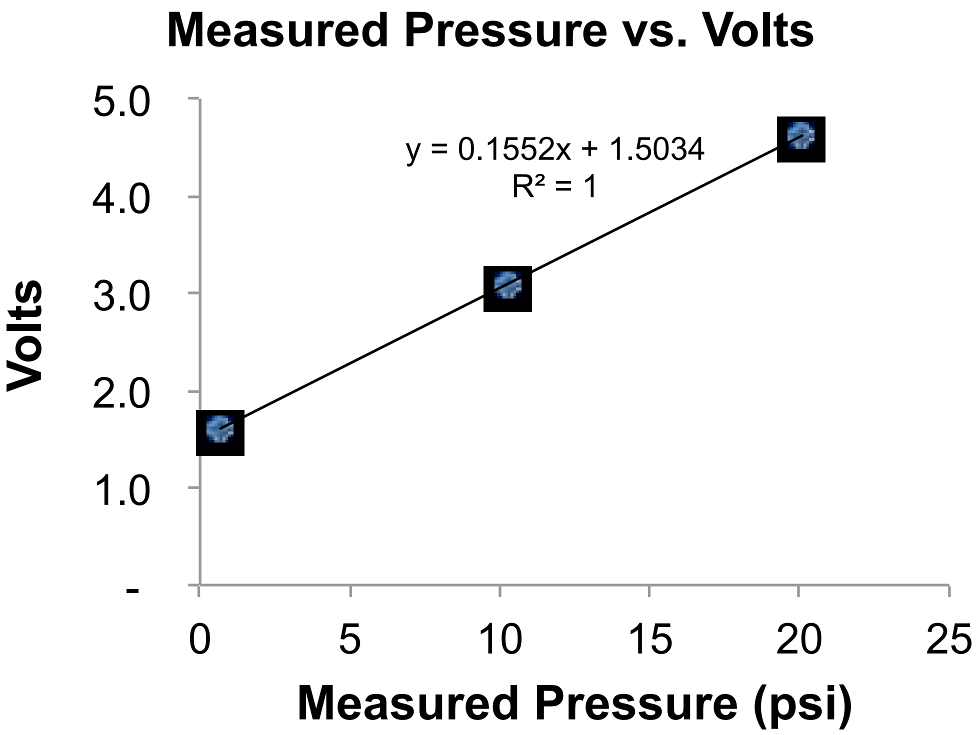


[redacted]

Using the parameter values originally input into the data acquisition system, seen in Table 6.1, a linear equation was constructed relating the voltage and the recorded flow read by the data acquisition system. Using this equation, the volts were calculated with the measured flow values obtained. Figure 6.2 shows this relationship.

Table 6.1: Initial parameters in data acquisition system

Volts	Pressure (psi)
1	0
5	25



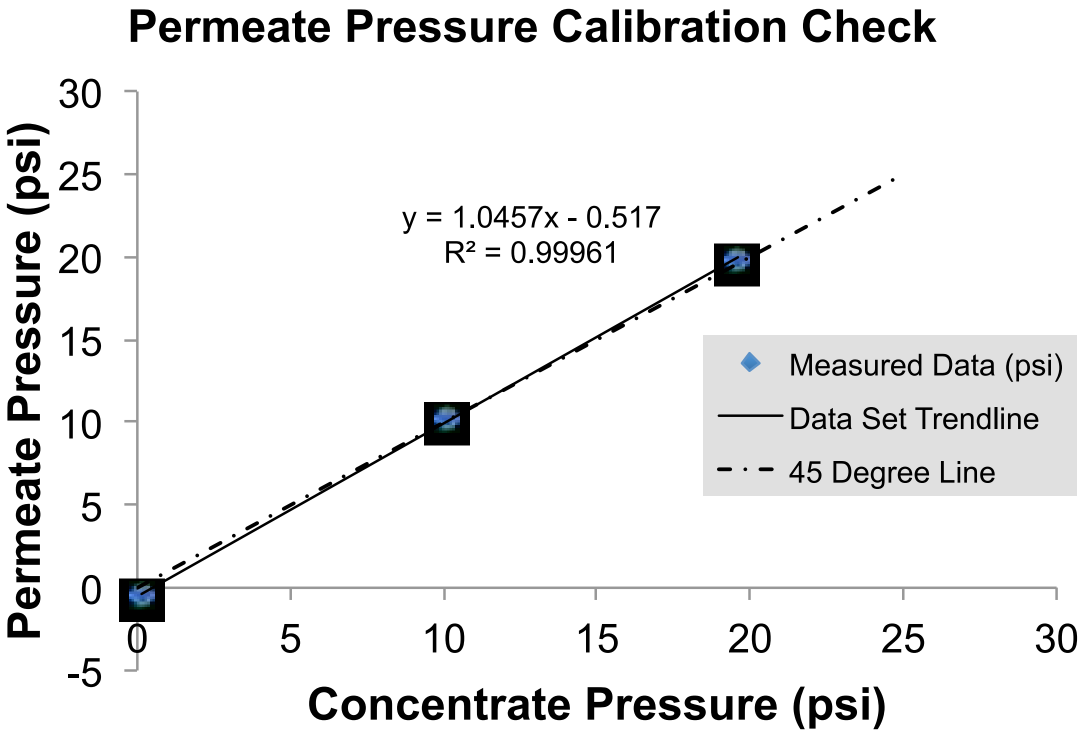
[redacted]

Using the trendline equation in Figure 6.2, new parameter input values were obtained by plugging in 0 psi and 25 psi into the equation. The new parameters can be seen in Table 6.2.

Table 6.2: Parameters entered into data acquisition system after calibration

Volts	Pressure (psi)
1.5034	0
5.3834	25

The new parameters were input into the data acquisition system and the calibration was checked by repeating the above method for the calibration. Figure 6.3 below shows this calibration check. Table 6.3 shows the error of the measurements at the various calibration points after the new parameters were entered in the data acquisition system. The calculated error was significantly better than the specified error of the instrument. The measured error is sufficient to record the permeate pressure to within 0.63 psi over the entire range.



[redacted]

Table 6.3: Accuracy of measurements after calibration of permeate pressure transducer

Measured Pressure (psi)	Recorded Pressure (psi)	Error (% of full scale)
0.14	-0.49	-2.50
10.07	10.24	0.70
19.60	19.86	1.04

Section 7: Calibration of the Type-K Thermocouple

Make/Model: Digi-Sense (Cole-Parmer)

SN: 08516-74

Date of Calibration by UNM: August 26, 2016

This Type-K thermocouple is used to measure the temperature in the feed tank. The calibration methods included spot checking the thermocouple at the boiling and freezing points of water. The temperature water boils at the elevation of Centennial Engineering Building on the University of New Mexico campus was calculated to be 202.5°F. A beaker filled with water was placed on a hot plate until the water started to boil. The thermocouple was placed into the boiling water and temperature recorded. The temperature for the freezing point of water used to check the calibration on the thermocouple was 32°F. Ice was placed into a beaker full of water. The ice was allowed to sit until it was no longer melting. At this time, the thermocouple was placed into the ice bath and the temperature recorded. The recorded temperature, or the thermocouple readings, can be seen in Table 7.1.

Table 7.1: Spot check of Type-K thermocouple

Recorded Temperature (°F)
199
32

Appendix B: Test Procedure for Ultra-Low Pressure Membranes

Membranes

1. **Dow Filmtec NF 270 (kw=16.65)**
2. **GE AP (kw=11.12)**
3. **+ one duplicate Dow Filmtec NF 270**

Phase One: DI cleaning and compaction

- Fill tank with DI water
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25m/s (set VFD to 12.6 Hz)
- Feed pressure kept at **highest pressure (6.89 bar, 100 psi)**
- Empty tank, refill with DI water at 2, 4, and 6 hours after start of test.
- Measure conductivity of feed tank after 6 hours to make sure membranes are clean
- Run for 24 hours

Phase Two: NaCl/boron rejection

- Fill tank with NaCl and boric acid solution
    - 20 L total of 2000 ppm NaCl and 5 ppm boron (as boric acid) solution
        - Add 40.00 g of NaCl and 0.5720 g boric acid
    - Add 3.8393 g NaH_2PO_4 (1.6 mM) and 1.1357 g Na_2HPO_4 (0.4 mM) to tank for phosphate buffer
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25m/s (set VFD to 12.6 Hz)
- Keep feed pressure at **medium pressure (5.17 bar, 75 psi)**
- Run for 24 hours
- **Take initial feed tank sample: measure conductivity, boron, and pH, using the procedure below**
- Sampling procedure for conductivity, boron, and pH:
    a. Take feed tank sample first, all five permeate samples (membrane 1 to membrane 3) second, and concentrate line sample last.
    b. Place waste beaker below sample port.
    c. Turn permeate valve to be sampled to the single permeate line. **Write time of which sample valve is opened in lab notebook!** Wait for about 3 minutes for flow to stabilize.
    d. Allow at least 20 mL to discharge into the waste beaker. This will be returned to the tank. The purpose of this is to clean the sample lines completely. The valves will never be closed during the sampling procedure.
    e. Collect samples for conductivity and pH in the three different small clean glass beakers, one each for the feed, concentrate, and permeate.
        a. Condition the beaker 2 times by collecting some sample, swirling it in the beaker, and pouring it into the waste beaker.

    b. Measure conductivity, then pH. Dump sample into waste.
    c. Rinse small glass beakers with DI water after sample measurements are taken, and set aside for next use.
  f. Collect boron samples in 20 mL plastic Nalgene bottle. Condition the bottle 2 times by collecting some sample, swirling it in the bottle, and pouring it into the waste beaker. These do not need to be headspace free, but fill completely.
  g. Close the sample valve and record the time that sampling was complete.
  h. Repeat steps b to h for the remaining sample locations.
  i. Dump the contents of the waste beaker back into the feed tank.

Phase Three: Organics rejection

- Fill tank with DI water, and run through system to clean lines
- Fill tank with organics solution (20 L total of organics solution)
    - **See table below for organics to add**
    - Add Add 3.8393 g NaH_2PO_4 (1.6 mM) and 1.1357 g Na_2HPO_4 (0.4 mM) to tank for phosphate buffer
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25m/s (set VFD to 12.6 Hz)
- Keep pressure at **highest pressure (15.5 bar, 225 psi)**
- **Take initial feed tank sample (triplicate) in 40 mL vials provided by Hall, and one to measure pH in about 20 mL glass beaker**
    - **Dilute feed tank sample twice (10:1 dilutions)**
    - Take initial feed tank sample in clean beaker. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials. Take 20 mL out using a 10 mL glass pipette twice, and put into another 200 mL volumetric flask, then fill up to line with DI water. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials. Take 20 mL out of this second volumetric flask using a 10 mL glass pipette twice, then fill up to line with DI water. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials.
- **Take only initial concentrate sample for organics! No others needed.**
- Sampling procedure for pH and organics:
  a. Take feed tank sample first, all five permeate samples (membrane 1 to membrane 3) second, and concentrate line sample last. Only take concentrate sample on the highest test pressure sample time.
  b. Place waste beaker below sample port.
  c. Turn permeate valve to be sampled to the single permeate line. **Open sample valve and write time of which sample valve opened in lab notebook!** Wait for about 3 minutes for flow to stabilize.
  d. Allow at least 20 mL to discharge into the waste beaker. This will be returned to the tank. The purpose of this is to clean the sample

lines completely. The valves will never be closed during the sampling procedure.

    e. Samples for organics analysis are to be taken in triplicate in 40 mL sample vials provided by Hall Environmental, and sent to Hall Environmental for analysis. These vials are **<u>not</u>** conditioned before sampling.
    f. Collect samples for pH in the three different small clean glass beakers, one each for the feed, concentrate, and permeate.
        a. Condition the beaker 2 times by collecting some sample, swirling it in the beaker, and pouring it into the waste beaker.
        b. Measure pH and dump sample into waste.
        c. Rinse small glass beakers with DI water after sample measurements are taken, and set aside for next use.
    g. Collect the sample for organics by placing the sample bottle with the sample line inside the bottle, near the bottom to minimize agitation of the sample and volatilization of the compounds during sample collection. Once the sample bottle is completely full, slowly withdraw the sample bottle from the sample tube so that the bottle remains full. Cap the bottle without trapping any air (headspace free). Repeat for the remaining vials.
    h. Close the sample valve and record the time that sampling was complete.
    i. Repeat steps b to h for the remaining sample locations.
    j. Dump the contents of the waste beaker back into the feed tank.

- Step down the pressure to the **<u>medium pressure (5.17 bar, 75 psi), wait one hour</u>** and repeat sampling procedure for pH and organics.
    - Do not sample the concentrate for the organics
- Step down the pressure to the **<u>low pressure (3.45 bar, 50 psi), wait one hour</u>** and repeat sampling procedure for pH and organics
    - Do not sample the concentrate for organics
    - On last sample (Permeate 3 sample) repeat sampling for organics 3 times total for test QA

Compound Mixes	**Spike Concentration (μg/L)**	**Amount Added to Tank**	**Number of Compounds in Mixes**
Mix 1	See spike solutions excel sheet	40 mL	6
Mix 2	See spike solutions excel sheet	10 mL	3
EPA Mix 1	250	Add one 1 mL ampule, and 1 1.5 mL ampule	53
EPA Mix 6	150	Add one 1.5 mL ampule	5

Membranes

4. **Hydranautics ESPA2-LD (kW=4.69)**
5. **Toray TMG(D) (kW=5.96)**
6. **Dow Filmtec BW30XFRLE (kW=5.59)**
7. **GE AG LF (kW=3.22)**
8. **+ duplicate of Hydranautics ESPA2-LD (kW=4.69)**

Phase One: DI cleaning and compaction

- Fill tank with DI water
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25 m/s (set VFD to 12.6 Hz)
- Feed pressure kept at **highest pressure (15.51 bar, 225 psi)**
- Empty tank, refill with DI water at 2, 4, and 6 hours after start of test.
- Measure conductivity of feed tank after 6 hours to make sure membranes are clean
- Run for 24 hours

Phase Two: NaCl/boron rejection

- Fill tank with NaCl and boric acid solution
    - 20 L total of 2000 ppm NaCl and 5 ppm boron (as boric acid) solution
        - Add 40.00 g of NaCl and 0.5720 g boric acid
    - Add 3.8393 g NaH_2PO_4 (1.6 mM) and 1.1357 g Na_2HPO_4 (0.4 mM) to tank for phosphate buffer for a pH of 6.5
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25 m/s (set VFD to 12.6 Hz)
- Keep feed pressure at **medium pressure (10.34 bar, 150 psi)**
- Run for 24 hours
- **Take initial feed tank sample: measure conductivity, boron, and pH, using the procedure below**
- Sampling procedure for conductivity, boron, and pH:
    j. Take feed tank sample first, all five permeate samples (membrane 1 to membrane 5) second, and concentrate line sample last.
    k. Place waste beaker below sample port.
    l. Turn permeate valve to be sampled to the single permeate line. **Write time of which sample valve is opened in lab notebook!** Wait for about 3 minutes for flow to stabilize.
    m. Allow at least 20 mL to discharge into the waste beaker. This will be returned to the tank. The purpose of this is to clean the sample lines completely. The valves will never be closed during the sampling procedure.
    n. Collect samples for conductivity and pH in the three different small clean glass beakers, one each for the feed, concentrate, and permeate.

        a. Condition the beaker 2 times by collecting some sample, swirling it in the beaker, and pouring it into the waste beaker.
        b. Measure conductivity, then pH. Dump sample into waste.
        c. Rinse small glass beakers with DI water after sample measurements are taken, and set aside for next use.
    o. Collect boron samples in 20 mL plastic Nalgene bottle. Condition the bottle 2 times by collecting some sample, swirling it in the bottle, and pouring it into the waste beaker. These do not need to be headspace free, but fill completely.
    p. Close the sample valve and record the time that sampling was complete.
    q. Repeat steps b to g for the remaining sample locations.
    r. Dump the contents of the waste beaker back into the feed tank.

Phase Three: Organics rejection

- Fill tank with DI water, and run through system to clean lines
- Fill tank with organics solution (20 L total of organics solution)
    - **See table below for organics to add**
    - Add 3.8393 g NaH_2PO_4 (1.6 mM) and 1.1357 g Na_2HPO_4 (0.4 mM) to tank for phosphate buffer for a pH of 6.5
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25 m/s (set VFD to 12.6 Hz)
- Keep pressure at **<u>highest pressure (15.51 bar, 225 psi)</u>**
- **Take initial feed tank sample (triplicate) in 40 mL vials provided by Hall, and one to measure pH and conductivity in about 20 mL glass beaker**
    - **Dilute feed tank sample twice (10:1 dilutions)**
    - Take initial feed tank sample in clean beaker. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials. Take 20 mL out using a 10 mL glass pipette twice, and put into another 200 mL volumetric flask, then fill up to line with DI water. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials. Take 20 mL out of this second volumetric flask using a 10 mL glass pipette twice, then fill up to line with DI water. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials.
- **Take concentrate sample at high pressure sampling time for organics! No other concentrate samples needed.**
- Sampling procedure for conductivity, pH, and organics:
    k. Take feed tank sample first, all five permeate samples (membrane 1 to membrane 5) second, and concentrate line sample last. Only take concentrate sample on the highest test pressure sample time.
    l. Place waste beaker below sample port.
    m. Turn permeate valve to be sampled to the single permeate line. **Open sample valve and write time of which sample valve**

opened in lab notebook! Wait for about 3 minutes for flow to stabilize.

n. Allow at least 20 mL to discharge into the waste beaker. This will be returned to the tank. The purpose of this is to clean the sample lines completely. The valves will never be closed during the sampling procedure.
o. Samples for organics analysis are to be taken in triplicate in 40 mL sample vials provided by Hall Environmental, and sent to Hall Environmental for analysis. These vials are **<u>not</u>** conditioned before sampling.
p. Collect samples for conductivity and pH in the three different small clean glass beakers, one each for the feed, concentrate, and permeate.
    a. Condition the beaker 2 times by collecting some sample, swirling it in the beaker, and pouring it into the waste beaker.
    b. Measure conductivity, then pH, dump sample into waste.
    c. Rinse small glass beakers with DI water after sample measurements are taken, and set aside for next use.
q. Collect the sample for organics by placing the sample bottle with the sample line inside the bottle, near the bottom to minimize agitation of the sample and volatilization of the compounds during sample collection. Once the sample bottle is completely full, slowly withdraw the sample bottle from the sample tube so that the bottle remains full. Cap the bottle without trapping any air (headspace free). Repeat for the remaining vials.
r. Close the sample valve and record the time that sampling was complete.
s. Repeat steps b to h for the remaining sample locations.
t. Dump the contents of the waste beaker back into the feed tank.

- Step down the pressure to the **<u>medium pressure (10.34 bar, 150 psi), wait one hour</u>** and repeat sampling procedure for conductivity, pH, and organics.
    - Do not sample the concentrate for the organics
- Step down the pressure to the **<u>low pressure (5.17 bar, 75 psi), wait one hour</u>** and repeat sampling procedure for conductivity, pH, and organics
    - Do not sample the concentrate for organics
    - On last sample (Permeate 3 sample) repeat sampling for organics 3 times total for test QA

Compound Mixes	**Spike Concentration (μg/L)**	**Amount Added to Tank**	**Number of Compounds in Mixes**
Mix A	See spike solutions excel sheet	40 mL	6
Mix B	See spike solutions excel sheet	10 mL	3
EPA Mix 1	300	Add three 1.0 mL ampules	53
EPA Mix 6	300	Add two 1.5 mL	5

		ampules	
EPA Mix 5	See WRRF Compound List excel sheet	Add one 1.5 mL ampule	6

Appendix D: Test Procedure for Seawater Membranes

Membranes

9. **Toray TM800M (kW=1.06)**
10. **Dow Filmtec SW30XHR (kW=0.92)**
11. **+ duplicate of Toray TM800M (kW=1.06)**

Phase One: DI cleaning and compaction

- Fill tank with DI water
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25 m/s (set VFD to 12.6 Hz)
- Feed pressure kept at **highest pressure (24.13 bar, 350 psi)**
- Empty tank, refill with DI water at 2, 4, and 6 hours after start of test.
- Measure conductivity of feed tank after 6 hours to make sure membranes are clean
- Run for 24 hours
- Take sample of feed tank after 24 hours for TOC analysis in 40 mL amber headspace free vial

Phase Two: NaCl/boron rejection

- Fill tank with NaCl and boric acid solution
    - 20 L total of 2000 ppm NaCl and 5 ppm boron (as boric acid) solution
        - Add 40.00 g of NaCl and 0.5720 g boric acid
    - Add 3.8393 g NaH_2PO_4 (1.6 mM) and 1.1357 g Na_2HPO_4 (0.4 mM) to tank for phosphate buffer for a pH of 6.5
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25 m/s (set VFD to 12.6 Hz)
- Keep feed pressure at **medium pressure (15.5 bar, 225 psi)**
- Run for 24 hours
- **Take initial feed tank sample: measure conductivity, boron, and pH, using the procedure below**
- Sampling procedure for conductivity, boron, and pH:
    s. Take feed tank sample first, all three permeate samples (membrane 1 to membrane 3) second, and concentrate line sample last.
    t. Place waste beaker below sample port.
    u. Turn permeate valve to be sampled to the single permeate line. **Write time of which sample valve is opened in lab notebook!** Wait for about 3 minutes for flow to stabilize.

v. Allow at least 20 mL to discharge into the waste beaker. This will be returned to the tank. The purpose of this is to clean the sample lines completely. The valves will never be closed during the sampling procedure.

w. Collect samples for conductivity and pH in the three different small clean glass beakers, one each for the feed, concentrate, and permeate.
   a. Condition the beaker 2 times by collecting some sample, swirling it in the beaker, and pouring it into the waste beaker.
   b. Measure conductivity, then pH. Dump sample into waste.
   c. Rinse small glass beakers with DI water after sample measurements are taken, and set aside for next use.

x. Collect boron samples in 20 mL plastic Nalgene bottle. Condition the bottle 2 times by collecting some sample, swirling it in the bottle, and pouring it into the waste beaker. These do not need to be headspace free, but fill completely.

y. Close the sample valve and record the time that sampling was complete.

z. Repeat steps b to g for the remaining sample locations.

aa. Dump the contents of the waste beaker back into the feed tank.

Phase Three: Organics rejection

- Fill tank with DI water, and run through system to clean lines
- Fill tank with organics solution (20 L total of organics solution)
  - **See table below for organics to add**
  - Add 3.8393 g NaH_2PO_4 (1.6 mM) and 1.1357 g Na_2HPO_4 (0.4 mM) to tank for phosphate buffer for a pH of 6.5
- Keep tank at constant temperature of 20 °C (68 °F)
- Keep feed velocity at 0.25 m/s (set VFD to 12.6 Hz)
- Keep pressure at **<u>highest pressure (24.13 bar, 350 psi)</u>**
- **Take initial feed tank sample (triplicate) in 40 mL vials provided by Hall, and one to measure pH and conductivity in about 20 mL glass beaker**
  - **Dilute feed tank sample twice (10:1 dilutions)**
  - Take initial feed tank sample in clean beaker. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials. Take 20 mL out using a 10 mL glass pipette twice, and put into another 200 mL volumetric flask, then fill up to line with DI water. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials. Take 20 mL out of this second volumetric flask using a 10 mL glass pipette twice, then fill up to line with DI water. Take 40 mL sample (three times because samples need to be in triplicate) in Hall provided sample vials.
- **Take concentrate sample at high pressure sampling time for organics! No other concentrate samples needed.**
- Sampling procedure for conductivity, pH, and organics:

    u. Take feed tank sample first, all three permeate samples (membrane 1 to membrane 3) second, and concentrate line sample last. Only take concentrate sample on the highest test pressure sample time.
    v. Place waste beaker below sample port.
    w. Turn permeate valve to be sampled to the single permeate line. **Open sample valve and write time of which sample valve opened in lab notebook!** Wait for about 3 minutes for flow to stabilize.
    x. Allow at least 20 mL to discharge into the waste beaker. This will be returned to the tank. The purpose of this is to clean the sample lines completely. The valves will never be closed during the sampling procedure.
    y. Samples for organics analysis are to be taken in triplicate in 40 mL sample vials provided by Hall Environmental, and sent to Hall Environmental for analysis. These vials are **<u>not</u>** conditioned before sampling.
    z. Collect samples for conductivity and pH in the three different small clean glass beakers, one each for the feed, concentrate, and permeate.
        a. Condition the beaker 2 times by collecting some sample, swirling it in the beaker, and pouring it into the waste beaker.
        b. Measure conductivity, then pH, dump sample into waste.
        c. Rinse small glass beakers with DI water after sample measurements are taken, and set aside for next use.
    aa. Collect the sample for organics by placing the sample bottle with the sample line inside the bottle, near the bottom to minimize agitation of the sample and volatilization of the compounds during sample collection. Once the sample bottle is completely full, slowly withdraw the sample bottle from the sample tube so that the bottle remains full. Cap the bottle without trapping any air (headspace free). Repeat for the remaining vials.
    bb. Close the sample valve and record the time that sampling was complete.
    cc. Repeat steps b to h for the remaining sample locations.
    dd. Dump the contents of the waste beaker back into the feed tank.

- Step down the pressure to the **<u>medium pressure (15.5 bar, 225 psi), wait one hour</u>** and repeat sampling procedure for conductivity, pH, and organics.
    - Do not sample the concentrate for the organics
- Step down the pressure to the **<u>low pressure (10.34 bar, 150 psi), wait one hour</u>** and repeat sampling procedure for conductivity, pH, and organics
    - Do not sample the concentrate for organics
    - On last sample (Permeate 3 sample) repeat sampling for organics 3 times total for test QA

Compound Mixes	Spike Concentration (µg/L)	Amount Added to Tank	Number of Compounds in Mixes
Mix A	See spike solutions excel sheet	40 mL	6
Mix B	See spike solutions excel sheet	10 mL	3
EPA Mix 1	300	Add four 1.0 mL ampules	53
EPA Mix 6	300	Add two 1.5 mL ampules	5
EPA Mix 5	See WRRF Compound List excel sheet	Add one 1.5 mL ampule	6

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