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STUDY OF THE RETENTION OF BISPHNEOL-A BY TWO NANOFILTRATION MEMBRANES OF DIFFERENT MOLECULAR WEIGHT CUT-OFF

Author: Aidan Harvey
Supervisor: José Marcial Gozálvez Zafrilla
María Asunción Santafé Moros

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Study of the Retention of Bisphenol-A by Two Nanofiltration Membranes of Different Molecular Weight Cut-offs

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In-house Supervisors: Prof. José M. Gozálvez Zafrilla, Prof. Asunción Santafé Moros

Academic Supervisor: Dr Edward Brightman

Summary

The primary aim of this report was to investigate the nanofiltration of Bisphenol-A (BPA) using two membranes of differing molecular weight cut-offs (MWCOs). This was in order to gain further understanding of BPA retention mechanisms, and study how the chosen membranes interacted with the molecules, with a view to application in industrial wastewater treatment plants (WWTPs).

BPA is an endocrine disrupting chemical which causes harm to animals and humans and is prevalent in the environment as a microplastic due to the degradation of plastic waste. As such, these microplastics can accumulate and are usually found in effluents from WWTPs. Current methods of BPA removal while effective, could be improved, and nanofiltration, a pressure driven process, is a viable technique to apply in these scenarios.

Two commercial membranes, NP030 (MWCO = 500-600 Da) and NF270 (MWCO = 200-300 Da), were selected for evaluation, and a literature review was carried out to assess previous research in the area of interest. Dominant nanofiltration retention mechanisms identified were size exclusion, Donnan exclusion, and salt effect on solution components and membrane pores. From this an experimental plan was created which tested the impact of pressure (4 and 8 bar), pH (6 and 8), and solution ionic strength (0, 1,000 and 2,000 mg/L of sodium chloride) on BPA retention.

Solutions of 1 mg/L BPA, some with additional feed components, were tested for both membranes in a Sterlitech stirred cell setup at the pre-selected conditions. High-performance liquid chromatography was carried out to analyse BPA content in the collected samples. This approach allowed retention of BPA to be calculated, and analysis to be conducted on results from different conditions.

NF270 was found to be the more effective membrane for the process, giving BPA retentions ranging from 46.8-91.4% across the conditions assessed, while NP030's maximum retention was only 40.9%, with most results found to be below 25%. Pressure and solution ionic strength were identified as being influential towards the retention of BPA, but pH had no impact in the range tested. An experiment carried out with NF270 and real wastewater showed promising results of 57.5% BPA retention but no clear trends were identified from comparison with similar experiments.

The results from this study can now be used to guide a comprehensive process of optimisation of BPA retention for both membranes, along with the potential targeted testing of other types of membranes. This could lay the groundwork for future studies into the possible implementation of nanofiltration in industrial WWTPs. It also provides a base of knowledge for any researcher investigating BPA removal through nanofiltration, and relevant experimental methods for any similar future studies.

Resum

L'objectiu principal d'este informe era investigar la nanofiltració de Bisfenol-A (BPA) utilisant dues membranes de diferents talls de pes molecular (MWCO). En això es pretenia conéixer millor els mecanismes de retenció del BPA i estudiar cóm les membranes elegides interactuaven amb les molècules, amb vistes a la seua aplicació en les estacions de tractament d'aigües residuals industrials (EDAR).

El BPA és un producte químic disruptiu endocrí que causa danys als animals i als sers humans i està present en el mig ambient com a microplàstic a causa de la degradació dels residus plàstics. Com a tal, estos microplàstics poden acumular-se i solen trobar-se en els efluents de les EDAR. Els métodos actuals d'eliminació de BPA, encara que són eficaços, podrien millorar-se, i la nanofiltració, un procés impulsat per la pressió, és una tècnica viable per a aplicar en estos escenaris.

Es varen seleccionar per a la seua evaluació dues membranes comercials, NP030 (MWCO = 500-600 Da) i NF270 (MWCO = 200-300 Da), i es va fer una revisió bibliogràfica per avaluar les investigacions anteriors en l'àrea d' interès. Els mecanismes de retenció de nanofiltració dominants identificats van ser l'exclusió per tamany, l'exclusió de Donnan i l'efecte de la sal en els components de la solució i els poros de la membrana. A partir d'açò es va crear un pla experimental que va provar l'impacte de la pressió (4 i 8 bar), el pH (6 i 8) i la força iònica de la solució (0, 1.000 i 2.000 mg/L de clorur de sodi) sobre la retenció de BPA.

Es varen provar solucions d'1 mg/L de BPA, algunes amb components d'alimentació adicionals, per a abdós membranes en una configuració de cela agitada Sterlitech en les condicions preseleccionades. Es va portar a terme una cromatografia líquida d'alt rendiment per analisar el contingut de BPA en les mostres arreplegades. Este enfocament va permetre calcular la retenció de BPA i analisr els resultats de diferents condicions.

La NF270 va resultar ser la membrana més eficaç per al procés, en retencions de BPA que oscilaven entre el 46,8 i el 91,4% en les condicions evaluades, mentres que la retenció màxima de NP030 va ser només del 40,9%, i la majoria dels resultats varen ser inferiors al 25%. La pressió i la força iònica de la solució es varen identificar com a influents en la retenció de BPA, però el pH no va tindre cap impacte en el rang provat. Un experiment realisat amb NF270 i aigües residuals reals va mostrar resultats prometedors de retenció del 57,5% de BPA, però no es varen identificar tendències clares en comparació amb experiments similars.

Els resultats d'este estudi poden utilitzar-se ara per a orientar un procés exhaustiu d'optimisació de la retenció de BPA per a abdós membranes, junt en el possible ensaig especific d'atres tipos de membranes. Açò podria assentar les bases per a futurs estudis sobre la possible aplicació de la nanofiltració a les EDAR industrials. També proporciona una base de coneixements per a qualsevol investigador que investigue l'eliminació de BPA per mig de nanofiltració, aixina com els métodos experimentals pertinents per a qualsevol estudi futur similar.

Resumen

El objetivo principal de este informe era investigar la nanofiltración del Bisfenol-A (BPA) utilizando dos membranas de diferente peso molecular (MWCO). Con ello se pretendía conocer mejor los mecanismos de retención del BPA y estudiar cómo interactuaban las membranas elegidas con las moléculas, con vistas a su aplicación en las plantas de tratamiento de aguas residuales industriales (EDAR).

El BPA es un producto químico perturbador endocrino que causa daños a los animales y a los seres humanos y que está presente en el medio ambiente en forma de microplásticos debido a la degradación de los residuos plásticos. Como tal, estos microplásticos pueden acumularse y suelen encontrarse en los efluentes de las EDAR. Los métodos actuales de eliminación del BPA, aunque son eficaces, podrían mejorarse, y la nanofiltración, un proceso impulsado por la presión, es una técnica viable para aplicar en estos escenarios.

Se seleccionaron dos membranas comerciales, NP030 (MWCO = 500-600 Da) y NF270 (MWCO = 200-300 Da), para su evaluación, y se llevó a cabo una revisión de la literatura para evaluar la investigación previa en el área de interés. Los mecanismos de retención de nanofiltración identificados fueron la exclusión por tamaño, la exclusión Donnan y el efecto de la sal en los componentes de la solución y los poros de la membrana. A partir de esto se creó un plan experimental que probó el impacto de la presión (4 y 8 bares), el pH (6 y 8) y la fuerza iónica de la solución (0, 1.000 y 2.000 mg/L de cloruro de sodio) en la retención de BPA.

Se probaron soluciones de 1 mg/L de BPA, algunas de ellas con componentes de alimentación adicionales, para ambas membranas en una configuración de celda agitada Sterlitech en las condiciones preseleccionadas. Se llevó a cabo una cromatografía líquida de alto rendimiento para analizar el contenido de BPA en las muestras recogidas. Este método permitió calcular la retención de BPA y analizar los resultados de las diferentes condiciones.

Se descubrió que la NF270 era la membrana más eficaz para el proceso, ya que daba retenciones de BPA que oscilaban entre el 46,8 y el 91,4% en todas las condiciones evaluadas, mientras que la retención máxima de la NP030 era sólo del 40,9%, y la mayoría de los resultados eran inferiores al 25%. La presión y la fuerza iónica de la solución se identificaron como influyentes en la retención del BPA, pero el pH no tuvo ningún impacto en el rango probado. Un experimento realizado con NF270 y aguas residuales reales mostró resultados prometedores de 57,5% de retención de BPA, pero no se identificaron tendencias claras a partir de la comparación con experimentos similares.

Los resultados de este estudio pueden utilizarse ahora para guiar un proceso exhaustivo de optimización de la retención de BPA para ambas membranas, junto con las posibles pruebas específicas de otros tipos de membranas. Esto podría sentar las bases para futuros estudios sobre la posible implantación de la nanofiltración en las EDAR industriales. También proporciona una base de conocimientos para cualquier investigador que investigue la eliminación de BPA mediante nanofiltración, así como los métodos experimentales pertinentes para cualquier estudio futuro similar.

Acknowledgements

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Finally, I would like to thank my family for always being there over the last five years, and my friends, especially Iona, Oliver, and Andrew, for making me laugh and keeping me motivated throughout all of university.

Table of Contents

Nomenclature Table

Nomenclature		Units
Volumetric Flux	j_v	m^3/m^{2}s
Intrinsic Permeability	k	m^2
Viscosity	μ	Pa s
Applied Pressure	ΔP	Pa
Thickness of Membrane	Δx	m
Feed Concentration	C_f	mg/L
Permeate Concentration	C_p	mg/L
Retention of First Permeate	R_1	%
Concentration of First Permeate	C_{p1}	mg/L
Concentration of Feed	C_{f0}	mg/L
Recovery of First Permeate	Y_1	Unitless
Retention of Second Permeate	R_2	%
Concentration of Second Permeate	C_{p2}	mg/L
Concentration of Final Retentate	C_{f2}	mg/L
Recovery of Second Permeate	Y_2	Unitless
Convective Impediment	K_c	Unitless
Diffusive Impediment	K_d	Unitless
Concentration	c	mg/L
Pore Velocity	V	m/s
Molecular Diffusivity	D_i	m^2/s
Universal Gas Constant	R	J/mol K
Temperature	T	K
Molecular Volume of Solute	V_s	m^3/mol
Steric Partitioning Coefficient	Φ	Unitless
Peclet Number	Pe	Unitless
Membrane Pore Radius	r_p	m
DSPM Predicted Retention	R_{DSPM}	%
Osmotic Pressure	$\Delta\pi$	Pa
Conductivity	Λ	µS/cm

Acronym Table

Acronyms			
BPA	Bisphenol-A	**PC**	Polycarbonate
WWTP	Wastewater Treatment Plant	**TDI**	Tolerable Daily Intake
EDC	Endocrine Disrupting Chemical	**PCB**	Polychlorinated Biphenyl
MWCO	Molecular Weight Cut-Off	**PAH**	Polycyclic Aromatic Hydrocarbons
MW	Molecular Weight	**NOM**	Natural Organic Matter
PWP	Pure Water Permeability	**PES**	Polyethersulfone
UPV	Universitat Politecnica de Valencia	**TFC**	Thin-Film Composite
ISIRYM	Industrial, Radiophysical and Environmental Safety	**DSPM**	Donnan-Steric Partitioning Pore Model
PROMETEO	Membrane Processes, Liquid Effluent Treatment and Optimization	**HPLC**	High-Performance Liquid Chromatography

List of Tables

List of Figures

1 Introduction and Project Aims

1.1 Introduction

Yearly the worldwide plastic industry's output increases, and with this, waste from this sector also grows. From the 1950s through to present day it's though that more than 8.3 billion tonnes of plastic have been produced with approximately 300 million tonnes of plastic waste being generated every year (1). Only 9% of plastic waste ever manufactured has been recycled, with the other 91% being either incinerated, disposed of in landfill or dumped in the open environment.

The properties which make plastics so desirable, such as their durability, chemical and thermal resistance, are also key to their long-term existence in the environment. When they do break down in the environment, it's into small fragments called microplastics (2). This happens as the plastic's polymer's fragment into small pieces less than 5 mm in size, which are then spread across different ecosystems. The cycle of the spread of microplastics is shown in Figure 1.1. Although microplastics can degrade in the environment, due to the vast quantities released, they are more likely to accumulate. Human consumption can be through a variety of manners such as contaminated water and crops, but also products which contain microplastics, i.e., toothpaste, and inhalation of polluted dust (3). Attempts to remove microplastics in wastewater treatment plants (WWTPs) while somewhat effective, usually lead to them being re-released via sludge used as fertilizer.

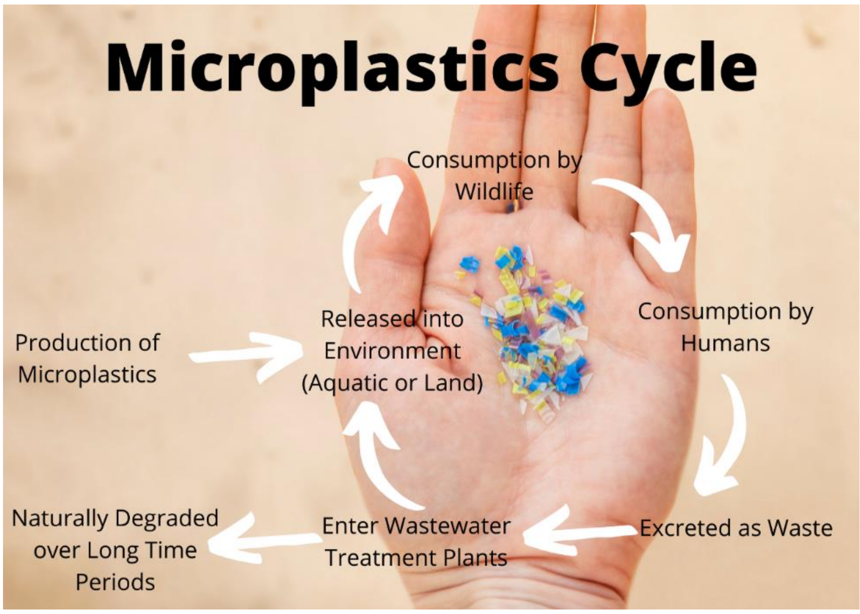


Figure 1.1: Microplastics Environmental Cycle

Microplastics are known to be dangerous to marine wildlife, as particles accumulate in fish, causing blocking of their digestive systems, growth inhibition and developmental damage (4). Meanwhile, microplastic hazards to humans are still unclear; studies have found evidence of potential effects such as an increased risk of cancer and disruption of the immune system, but further research is required (5).

The microplastic being studied in this report is Bisphenol-A (BPA), which is a manmade endocrine disrupting chemical (EDC) used to produce plastics. It's considered toxic and dangerous to both humans and animals. Its effects on humans are not universally agreed upon, but it’s though BPA can cause issues in the brain and prostate glands of children, with studies also highlighting potential links to increased blood pressure, heart disease and some cancers (6).

The aim of this report is to assess BPA removal from solutions using two nanofiltration membranes, at concentrations analogous to those in WWTPs. The membranes assessed were NP030 (Nadir™), a polyethersulfone (PES) based membrane, and NF270 (Dupont™), a polyamide-based membrane. The evaluation was mainly focalised on the second membrane due to the progression of the results obtained. It was hoped that the first screening of experimental factors performed in this study could aid in future experimental plans to set optimal conditions for BPA retention, hence aiding in developing effective techniques for application in industrial WWTPs. Experiments were carried out in conjunction with a membrane-separation research group at the Universitat Politecnica de Valencia.

Research of literature found studies on BPA removal using a variety of different nanofiltration membranes; polyamide membranes are generally the most commonly tested (7). Some PES membranes have been examined, however NP030 was untested on BPA solutions, creating an area of interest. With regards to NF270, while data has been collected on its retention of BPA, there is little consistent information on the effect varying experimental factors has on retention. The two membranes ultimately chosen for analysis have close molecular weight cut-offs (MWCO), which allowed for analysis between them and their retentions.

1.2 Project Aims and Description

The aims set out for the project, as agreed with the project supervisors, were:

1. To research previous studies using BPA in nanofiltration and screen a selection of membranes for use in experimental investigations.
2. To evaluate the chosen membranes in a stirred cell setup, to allow for the analysis and comparison of observed BPA retentions.
3. To study typical conditions for BPA retention by varying the following factors: solution ionic strength, solution pH, and cell pressure.

Alongside this, personal aims were made, which were:

1. Improve my working methods in a practical environment using laboratory equipment.
2. Gain a comprehensive and in-depth understanding of nanofiltration of micropollutant compounds, and the mechanisms for their removal from water solutions.
3. Improve communication, teamwork, and project management skills and gain experience in an academic environmental setting in preparation for postgraduate studies.

The report begins by providing a description of the target compound, BPA, and its environmental impact along with theory of nanofiltration, and molecular retention mechanisms. The methodology followed for experimental procedures is described, and the experimental results presented. These are analysed and compared to literature findings, before conclusions are drawn and a review of the overall project experience is provided, together with areas for future study.

2 Description of Organisation

This project was undertaken in conjunction with the Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM) of the Universitat Politecnica de Valencia. This institute incorporates electrochemical, nuclear, and biological knowledge alongside chemical engineering fundamentals to research areas of safety and environmental engineering. Of their four research groups, the Membrane Processes, Liquid Effluent Treatment and Optimization (PROMETEO) group provided the opportunity to carry out these experiments. Their focus is on separation of contaminants from liquid effluent, usually through membrane processes, and methods for clean water production. The data acquired through this study will be used to further their collective knowledge of interactions between trace organic compounds and nanofiltration membranes, and their achievable separations.

3 Background

3.1 Bisphenol-A

BPA is an organic compound that is used as an additive to produce resins such as polycarbonate (PC), Figure 3.1, and epoxy resin, which are then used in the production of plastics (8). These plastics are widely used due to their durability, with PC being utilised as solid food and drink containers, and epoxy resins used for coating cans and pipes. Yearly worldwide production of BPA has recently been reported to be approximately 2.72 million tonnes (9), with 95% of this used in the production of these two resins (10). Outwith of plastics BPA is also found in thermal paper.

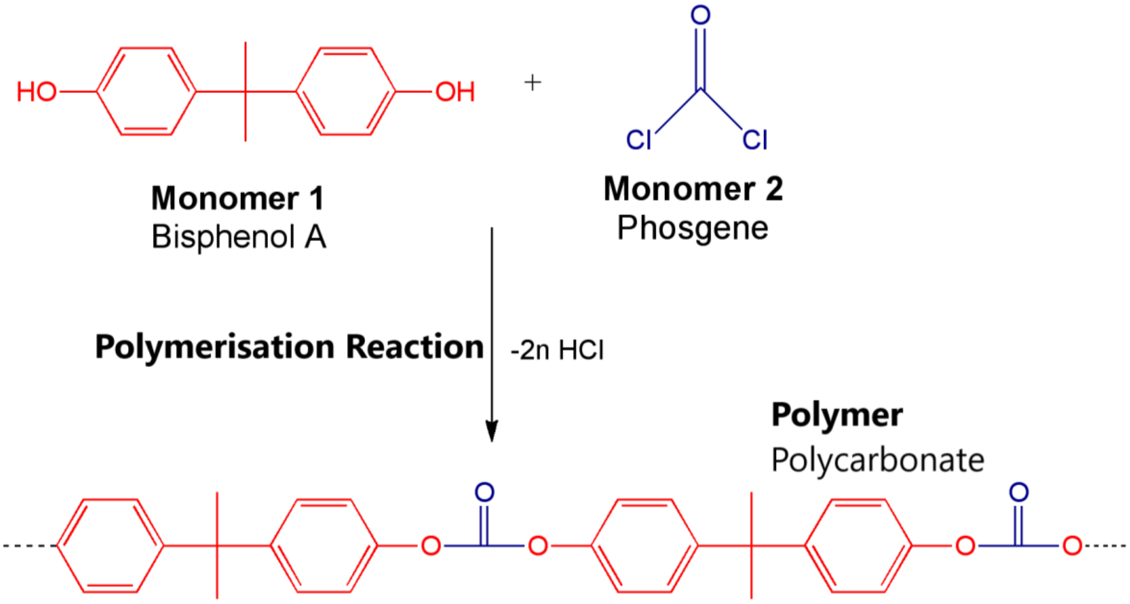


Figure 3.1: Reaction of BPA and Phosgene Producing Polycarbonate (11)

Despite its advantageous uses, BPA is known to be an EDC, meaning it's toxic and dangerous to both humans and animals (6). It mimics the effect of the hormone oestrogen, with exposure considered to cause developmental and reproductive issues (8). The recommended tolerable daily intake (TDI) is 0.004 mg/kg of body weight (12), with human current average daily intake being three to five times less than this value.

Annual estimates of BPA emissions to the environment are 455 tonnes (13). This can be from a variety of sources: leaching into soil from landfill, or effluent from productions plants and WWTPs (14). While this usually leads to BPA being present in water and soil, emissions to air are possible if products containing BPA are burned (15). The most probable route to human ingestion is through leaching from food containers. Main factors that impact BPA leaching are temperature, pH of contents, and age of the plastic; exposure to high heat and strong acidic or basic environments leads to hydrolysis of polymer intermolecular bonds (14). If subject to a small dose, the human body can quickly eliminate BPA by metabolization in the liver, but exposure to large doses can lead to accumulation in the body (16).

3.2 Plastic Waste Currently in the Environment

Approximately 14 million tonnes of plastic waste is released into oceans annually (17). Plastic degradation usually follows a three-step mechanism: photodegradation, thermo-oxidative degradation and biodegradation (18). This process uses energy from sunlight to initiate photodegradation, but the full cycle can take up to 50 years, and even longer in ocean environments due to lower temperatures. Figure 3.2 shows the process.

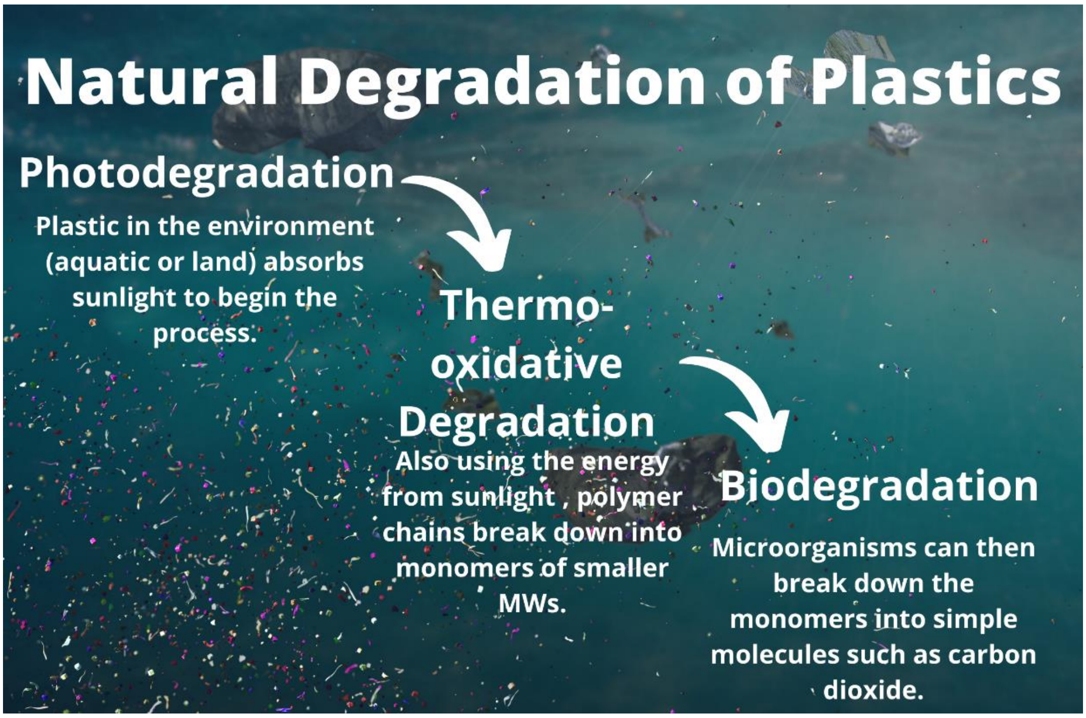


Figure 3.2: Plastic Degradation Process

As a result of this, many types of toxins as well as BPA can accumulate in water such as polychlorinated biphenyl's (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Alongside plastic degradation, there is the case where organic chemicals can adsorb onto plastic waste in water environments (19). This is seen with PCBs, as despite them being banned in many countries, they still cause legacy pollution issues (20). PAHs are also common in aquatic life as they accumulate on plastic debris. BPA is known to leach from PC in aquatic environments, with high rates found in the first 20 days after initial production (21).

Levels of BPA found in WWTPs are shown in Table 3.1. While some of this originates from human waste, high quantities of it are estimated to arise from industrial discharges (22). BPA degrades during wastewater treatment processes; however, residual amounts are still found to be discharged to fresh waters. Biosolids, another WWTP product, are used as fertilizer which presents another potential human exposure pathway.

Table 3.1: BPA Environmental Concentrations

Source	BPA Concentration (mg/L)	Reference
Hazardous Waste Landfill Leachate (Japan)	17.2	(23)
Paper Mill (Spain)	0.187	
Paper Manufacturer (Japan)	0.370	
WWTP (UK)	0.00111	(24)
River Water (China)	0.00392	
Industrial Effluents (Canada)	0.1492	
Seawater (Germany)	0.000249	
WWTP (USA)	0.00579	(25)
WWTP (Brazil)	0.00620	(26)

BPA is biodegradable with a half-life of 7 days or less in aquatic environments (27), but due to its widespread use, it's still commonly detected in wastewater. Methods for its removal are: activated sludge processes, biological aerated filtration, lagoon treatment, and primary treatment (26). Removal via a membrane bioreactor is a novel treatment not currently used on the same scale as the aforementioned methods (28). Sludge systems are found to have both chemical and biological removal effects, but this method isn't viable if the sludge's intended use is for fertilizer.

3.3 Filtration

Filtration is defined as a physical separation process which separates solids from liquid and gaseous phases, either mechanically, biologically, or physically. Over time as more microplastics enter the environment, it has become more crucial for effective filtration methods to be developed to remove pollutants. Table 3.2 and Figure 3.3 show different types of filtration.

The key principles for filtration are pore flow and diffusion. Pore flow dominates microfiltration and ultrafiltration, where pore sizes are large. In water purification scenarios, the larger particles cannot enter the pores, and the remaining solution passes though the membrane, giving high flowrates. These forms of filtration are carried out at low pressures.

Table 3.2: Types of Filtration (29–31)

Type of Filtration	Pore Size Ranges (nm)	Pressure Ranges (bar)	Typical MWCO (Da)
Microfiltration	100 – 10,000	0.1 – 5	500,000 – 1,000,000
Ultrafiltration	10 – 1,000	0.1 – 5	1,000 – 500,000
Nanofiltration	1 – 50	8 – 40	200 – 1,000
Reverse Osmosis	Non-porous – 1nm	30 – 85	<200

When purer water is required, nanofiltration and reverse osmosis must be utilised. Here diffusion from low concentration to high concentration is achieved via applying pressure to the system, which forces water through the membrane as permeate and leaves pollutant compounds in the retentate. This is a more intense process, giving lower flowrates but in return for a higher quality product.

BPA is a molecule that should theoretically be retained by membranes in the nanofiltration pore size range. While it's known it can be easily retained by reverse osmosis, these processes are intense due to the high pressures required, so it would be favourable to find nanofiltration conditions that give comparable BPA retentions at milder conditions.

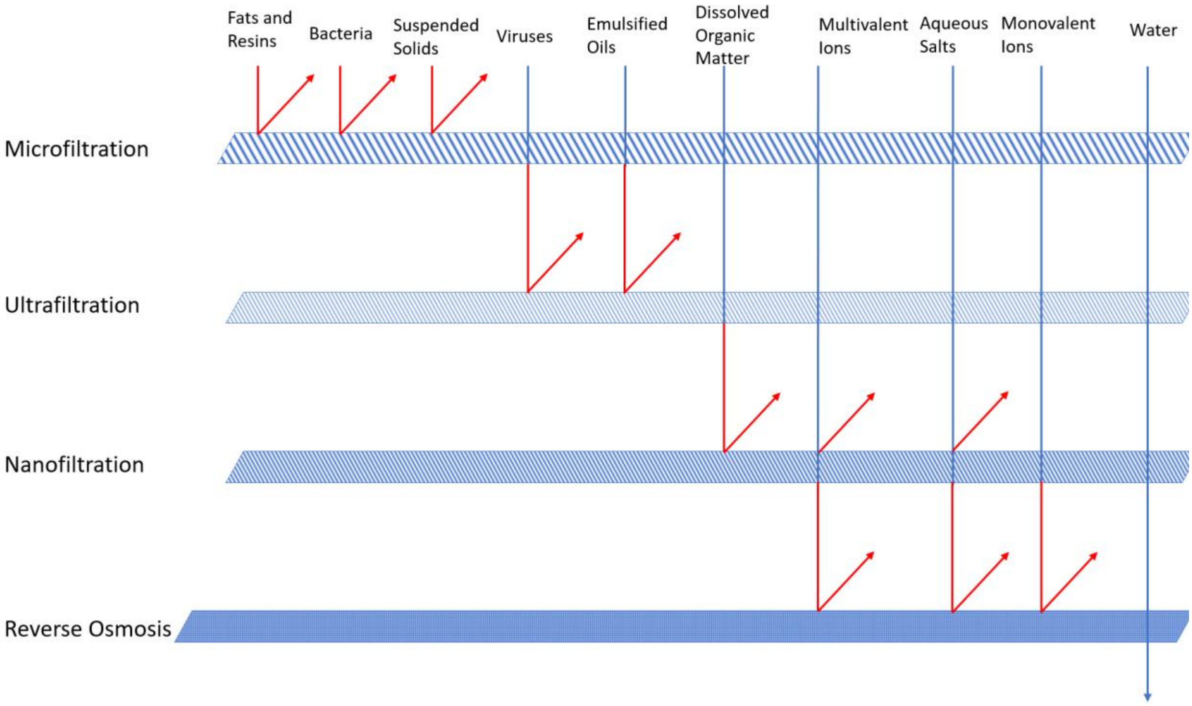


Figure 3.3: Types of Filtrations (29–31)

3.4 Nanofiltration

Nanofiltration is found to give high quality permeate though removal of organic compounds with molecular weights (MW) greater than 200 Da, using lower pressures than in reverse osmosis processes (32).

The MWCO of a membrane is the molecular weight of a standard component that is retained at 90% or more by that particular membrane (33). Membranes in the nanofiltration range have MWCO ranges of 200–1,000 Da (34) and as BPA has a MW of 228.29 g/mol (35), nanofiltration is well suited for this application. MWCOs are commonly assessed using salts or sugars, thus they are not always accurate sources for retention predictions.

Currently nanofiltration is mainly used in water softening and pesticide removal processes but has the potential to be used either at the end of wastewater treatment to give a pure effluent with little bacteria or dissolved compounds, or to treat process waters from sludge treatment activities. It would be useful for this second possibility, as it would prevent accumulation of organic compounds such as BPA in the sludge units.

Nonetheless, membrane fouling is a common nanofiltration problem which leads to membranes requiring replacement or cleaning, both at a cost (36). As most membranes are somewhat hydrophobic, this leads to other hydrophobic compounds adsorbing to their surface and causing complications. To avoid this, doping of chemicals onto the membrane active layer can be carried out as a method of prevention.

3.5 Types of Membranes

The two types of membranes tested in this report are thin-film composite (TFC) polyamide membranes and PES membranes. Other membranes such as cellulose and ceramic types are also commercially available.

Polyamide membranes are used for drinking water applications, with MWCOs usually in the range of 200-300 Da (37). Their structure consists of a dense surface layer, above a porous layer. The initial film prevents any hydrophobic interactions between the membrane and molecules in solution, which reduces surface adsorption (7). Frequent cleaning of polyamide membranes, while required, can damage the membrane active layer and lead to reduced retention of neutral organic chemicals such as BPA.

PES membranes while being strong and having a high thermal resistance, are more susceptible to fouling, due to their relatively higher hydrophobicity. To combat this, membrane surfaces can be modified to give them a more hydrophilic nature. This has been attempted in conjunction with BPA retention and been shown to increase it from 70% to 90% (32).

The contact angles of membranes give an indication of their hydrophobicity. As the contact angle increases, hydrophobicity of the membrane also increases, and subsequently the permeability of the membrane decreases. NP030 is found to be a more hydrophobic membrane than NF270 (38). EDCs are generally observed to be hydrophobic, which can aid in their adsorption to the polyamide membrane's polymers (7).

In literature, polyamide membranes give better retention of BPA than other types (7), albeit the best performances are from membranes with MWCOs in the reverse osmosis range. Although not tested here, ceramic membranes are an interesting prospect for future work due to their durability (37).

3.6 Flux and Retention

Darcy's Law, Equation 3.1 (39), shows that the fluid flux, j_v, through a membrane is proportional to the pressure applied, ΔP. The intrinsic permeability, k, and the thickness, Δx, are characteristics of the chosen membrane, and viscosity, μ, relates to the fluid undergoing filtration. Thus, at higher pressures, flux should increase. As membranes undergo fouling throughout their use, this decreases their permeability, which in turn reduces the flux through the membrane. Similarly, as filtration takes place, the solute concentration in the feed increases which leads to the osmotic pressure, $\Delta\pi$, increasing, and flux decreasing if pressure applied remains constant, see Equation 3.2.

$$j_v = \frac{-k}{\mu}\frac{\Delta P}{\Delta x} \qquad \text{Equation 3.1}$$

$$j_v = L_P(\Delta P - \Delta\pi) \qquad \text{Equation 3.2}$$

Retention represents the amount of a component that is prevented from moving through the membrane from the feed solution into the permeate. In the case of a differential membrane element (extremely low recovery) the fractional retention of one component is calculated using Equation 3.3. C_f is feed concentration and C_p is permeate concentration.

$$Retention\ (\%) = \frac{C_f - C_p}{C_f} \text{ x } 100 \qquad \text{Equation 3.3}$$

The retention of uncharged molecules can be estimated using the Donnan Steric-Partitioning Pore Model (DSPM) which accounts for steric hinderance, convection from applied pressure and diffusion due to concentration gradients, see Equation 3.4 (40). The third term including the pressure gradient is usually neglected to simplify the model as it's much smaller than the other contributions, giving the simplified Equation 3.5 (41). Nomenclature not yet defined for the following equations is shown in Table 3.3.

$$j_V = K_c\, c\, V - K_d\, D_i \frac{dc}{dx} - \frac{c\, K_d\, D_i}{RT} V_s \frac{dP}{dx} \qquad \text{Equation 3.4}$$

$$j_V = K_c\, c\, V - K_d\, D_i \frac{dc}{dx} \qquad \text{Equation 3.5}$$

Table 3.3: DSPM Nomenclature

Parameter	Symbol	SI Unit
Convective Impediment	K_c	Unitless
Diffusive Impediment	K_d	Unitless
Concentration	c	mol/m^3
Pore Velocity	V	m/s
Molecular Diffusivity	D_i	m^2/s
Universal Gas Constant	R	J/mol K
Temperature	T	K
Molecular Volume of Solute	V_s	mol/m^3
Uncharged Solute Steric Partitioning Coefficeint	ϕ	Unitless
Pore Radius	r_p	m
Membrane Permeability	L_p	m^3/m^2 s Pa

This can then be integrated across the concentration gradient of the membrane pore to gain an expression describing the retention of molecules. This is seen in Equation 3.6, with the Peclet number, *Pe*, shown in Equation 3.7.

$$R_{DSPM}\ (\%) = \frac{1-K_c\phi}{1-(1-K_c\phi)e^{-Pe}} \text{ x } 100 \qquad \text{Equation 3.6}$$

$$Pe = \frac{{K_c}^2\, {r_p}^2}{8\, L_p\, K_d\, D_i\, \mu\, j_v} \qquad \text{Equation 3.7}$$

This equation allows estimation of BPA retention with and without the presence of salt, using values of the Stokes radius of BPA and the average pore size of each membrane.

3.7 Membrane Retention Mechanisms Relating to BPA

In operation, it's observed that size exclusion is the primary mechanism that controls molecular permeation in nanofiltration. As such, molecules which are larger than the membrane's MWCO should be retained and not detected in the permeate, see Figure 3.4. Tight membranes are found to give greater retention of BPA than loose membranes, agreeing with this theory (42). If molecules larger than the MWCO are found in the permeate, then other factors must be considered.

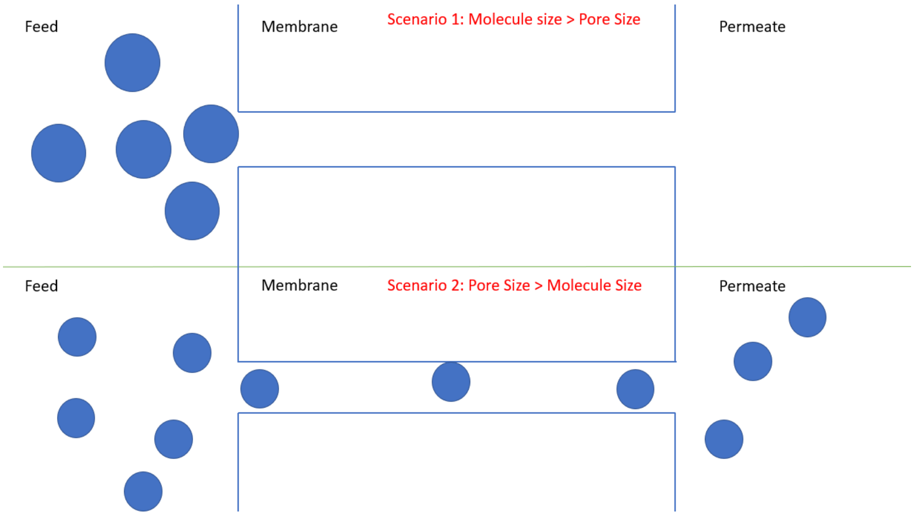


Figure 3.4: Size Exclusion Principle

The membrane and target molecule's affinity for water can influence the retention in these processes. In the case of BPA, it's a hydrophobic molecule, and the two membranes being tested are categorised as hydrophilic, although NF270 more so than NP030. Consequently, little adsorption of the component to NF270 is expected, although some would be anticipated for NP030. Furthermore, due to BPA's hydrophobic nature, it should have a smaller molecular size in an aqueous solution than its normal size, which may explain experimental retentions being poorer than predicted (42).

In practise, BPA adsorbs from the feed onto the membrane surface, increasing the concentration polarisation phenomenon (43), see Figure 3.5. The absorbed layer on the surface results in a concentration gradient, which leads to diffusion into the permeate. For large BPA concentrations, adsorption is quick and not noticeable. For smaller concentrations ($<1\text{x}10^{-6}$ mg/L) the effect is witnessed, with it seen that BPA retention decreases from an initial maximum to a steady value over time (43). If fouling of the membrane arises, this effect can also occur via build-up of BPA in a cake layer (44). Therefore, it's key to soak the membrane in BPA solutions prior to experiments, and calculate retention after a period of membrane climatisation (45). It's reported that increasing feed BPA concentration leads to a decrease in retention (46); this could be related to the concentration polarisation effect, but importantly emphasises the need to carry out BPA retention experiments at levels comparable to WWTPs.

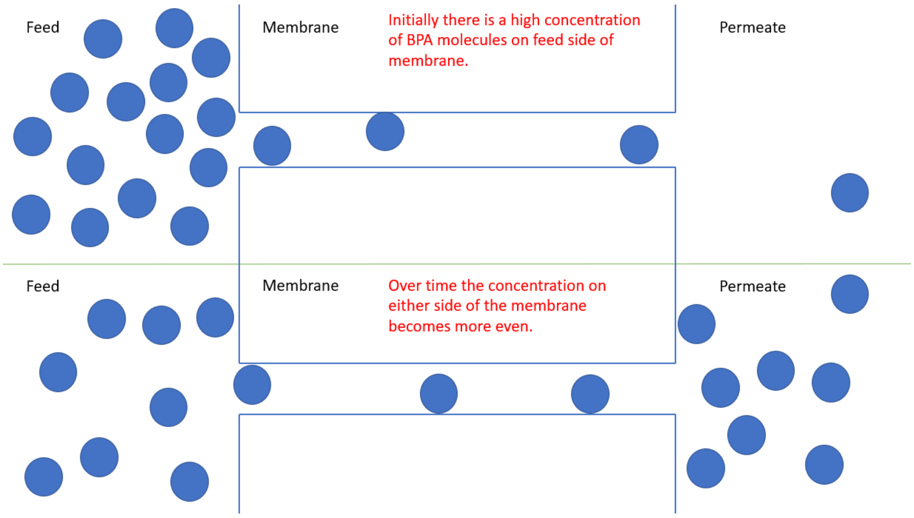


Figure 3.5: Concentration Polarisation Principle

Electrostatic interactions also affect retention through molecular charges. As BPA has a pKa value of between 9.6-10.2, it exists as a neutral molecule below pH 9.6 (7). When pH increases above this, it dissociates and becomes negatively charged. Meanwhile, NF270 and NP030 membranes are negatively charged (38,47). Thus, at neutral pH conditions, BPA adsorbs to the membrane surface with negligible repulsion forces. When pH increases beyond 9.6, there is repulsion between BPA molecules and the membrane, preventing surface adsorption and hence reducing diffusion to the permeate, shown in Figure 3.6. This is named the Donnan exclusion principle. It has been proven experimentally using NF270, at pH 8 and 11, with retention increasing from 45% to 95% (42). However, most WWTP processes operate in a pH range of 7-8, so this may not be practical.

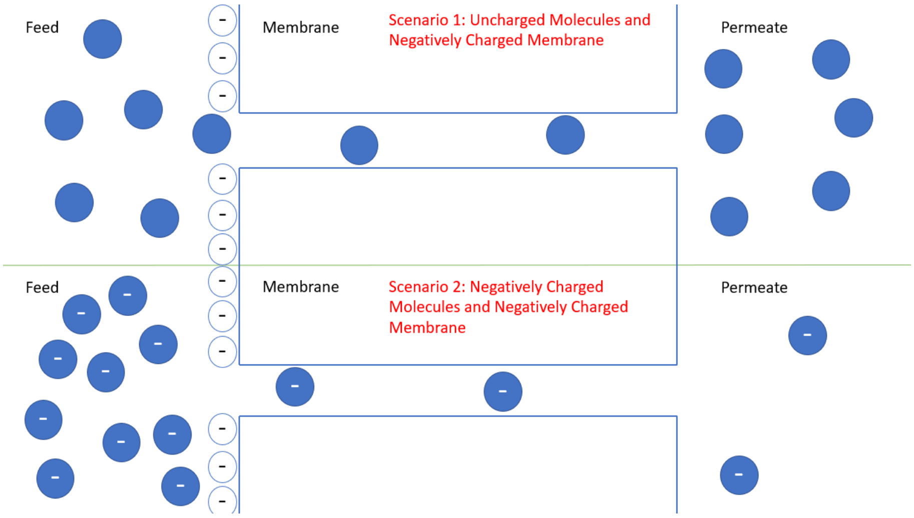


Figure 3.6: Donnan Exclusion Principle

In industry ionic strength of wastewaters due to total dissolved solids ranges from 840-12,100 mg/L (48), thus, inclusion of these compounds must be considered. The ionic strength of solutions can be altered by adding salts such as sodium chloride (NaCl), although this is thought to have a negative impact on retention. High concentrations of salts may cause the membrane pores to swell, due to an increase in counter-ion concentrations at the surface of the pores which in turn makes pores larger and thus easier for molecules to permeate through. Meanwhile, the salts will be more readily solvated by water, meaning BPA molecules will become compacted, decrease in size and pass more easily to the permeate (43), see Figure 3.7.

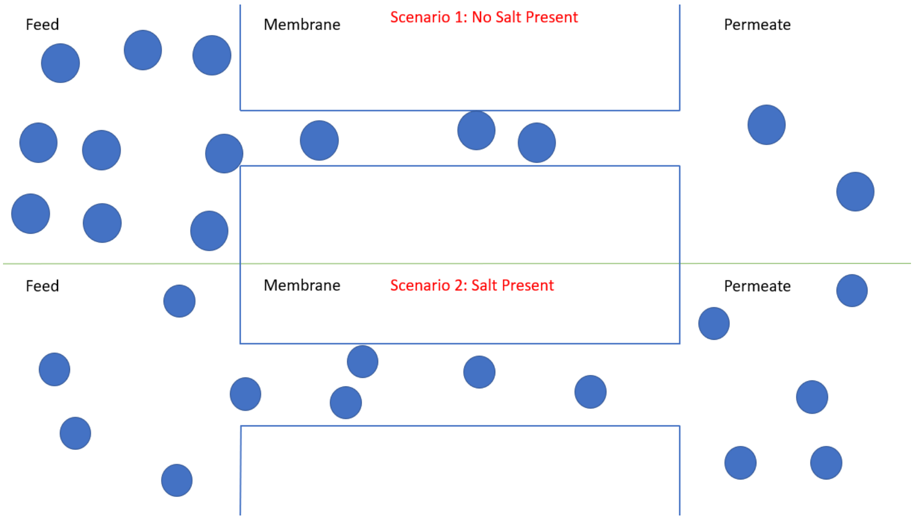


Figure 3.7: Ionic Strength Effect

As well as salts, solutions for nanofiltration experiments can be doped with natural organic matter (NOM) to try and increase compound retentions, as it can interact with both solutes and membranes. EDCs have been found to bond with NOM which leads to retention of both components via size exclusion or electrostatic repulsion (49). When used with salts, it's believed increased ionic strength influences NOM functional groups, thus altering NOM interactions with the membrane. Due to this NOM experiences less charge repulsion with the membrane surface, meaning it absorbs more readily and fouls the membrane (42). This layer then reduces the quantity of BPA that adsorbs to the membrane and limits the concentration polarisation effect. The combination of salts and NOM has previously gave small increases in BPA retention (42).

A deliberate effect can be employed, where the membrane is fouled to ensure that BPA retention increases. This has been observed when humic acid was used to foul a NF270 membrane, giving 45% BPA retention before and approximately 60% afterwards (44). The humic acid blocked the pores of the membrane, reducing their effective diameter, and formed a layer on the membrane surface, preventing BPA from diffusing through. In this scenario size exclusion is undeniably the prevalent factor in retention. Nonetheless, despite its apparent advantage, fouling is an extremely unwanted occurrence as it leads to more downtime and depending on the fouling it may either be irreversible, or the methods for cleaning it will damage the membrane structure, rendering it unusable.

BPA's structure is shown in Figure 3.8 and is seen to include two phenol groups. These aid in BPA adsorption to polymeric membranes, due to giving the molecule a relatively increased ability to undergo hydrogen bonding. This in conjunction with the surface of the membrane having net proton acceptor characteristics, leads to lower retentions than expected for neutral molecules (37).

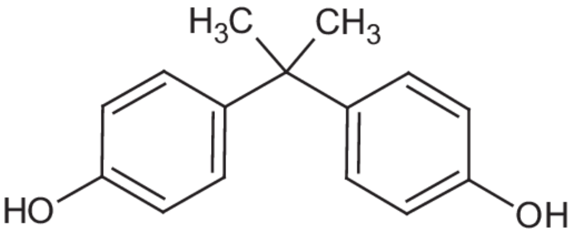


Figure 3.8: Molecular Structure of BPA (50)

A full literature review was conducted into experimental studies of nanofiltration of BPA, and this was used to focus the project's research. Table 3.4 summarises this review.

Table 3.4: BPA Removal Literature Review

BPA Concentrations (mg/L)	Pressure (bar)	Samples	pH	Membranes Used	Retentions in each Membrane (%)
50	10	Deionised water solutions spiked with BPA.	6 – 6.5	NF 90, NF 270, XLE BWRO, BW 30 CE BWRO and AD SWRO	Generally, >80% retention for each membrane. CE BWRO performed poorly giving retention of approximately 15%. NF270 gave retention around 80% (7).
5; 50; 100; 500	5.5	Deionised water and wastewater solutions spiked with BPA. Wastewater contained NOM.	5; 8	Modified and unmodified PES hollow fibre membranes.	For the modified PES with model solutions, approximately 70% retention for 5 mg/L and 50 mg/L samples, and lower for other two solutions. Unmodified PES gave lower retentions for each concentration. Greater retention observed at higher pH when using wastewater samples with the modified PES (32).
0.75	13	Electrolyte solution, containing 20 mM NaCl, 1 mM $CaCl_2$, and 1 mM $NaHCO_3$, and spiked with BPA.	8	NF-90, NF-270, and TFC-SR	90% retention for NF90, 45% for NF270 and 0% for TFC-SR2. Retention of BPA for all three membranes increased when they were tested in a humic acid fouled membrane (51).

		Humic acid used to foul membrane.			
0.1	5	Deionised water solutions spiked with BPA.	7	XLE and SC-1300.	XLE gave 83% retention, SC-1300 gave 18% (33).
0.00207	10 and 3.4	Deionised water solution spiked with BPA, lake water with EDCs present, and effluent from an MBR.	N/A	NF270, TS80 and X20.	X20 gave 96% retention, TS80 gave 25.6% and NF270 gave 4.6%, from the deionised water sample. Membrane fouling was seen in the samples from lake water, which increased the retention (49).
0.5	12	Deionised water solutions spiked with BPA. NOM and NaCl used.	6; 11	NF270 and NF90.	NF270 gave 40% retention and NF90 gave 90%. When tested in pH 11, NF270 gave much greater retention (90%). No difference was seen in the NF270 retention when ionic strength was increased. Slightly higher retention in NF270 seen when tested with increased ionic strength and the presence of NOM (42).
0.1	5.5	Deionised water solutions spiked with BPA.	7	ESNA and RO-XLE.	ESNA gave 45% retention, RO-XLE gave 90% (52).

0.001; 0.005; 0.01	20	Deionised water solutions spiked with BPA. NOM and NaCl used.	5 – 6	Desal 5 DK.	From 45% retention for 0.001 mg/L solution, to 60% for 0.01 mg/L. At high ionic strength, retention was poorer, although when the weakest ionic strength gave slightly better retention than the standard model solution. Experiments showed that NOM caused a faster decrease in BPA retention but had no effect on final retention (43).
0.05	3	Deionised water solutions spiked with BPA. Leachate used to provide NOM.	7	UTC60, NTR 729HF, ES10C, UTC70, LF10.	99% retention for all membranes except UTC60, which had a retention of 47%. Retention increased slightly at higher pressures, but had little influence on compounds with already high retentions (>99%) (53).
0.5 - 3	4 – 12	Deionised water solutions spiked with BPA. KCl used.	N/A	Only specifies - “from Toray, Japan”.	90% retention for lowest concentration, decreasing to 81% for strongest concentration. Increasing pH from 4 to 8 gave a decrease in retention but increasing it beyond 8 led to retention increasing. Increasing ionic strength was found to bring about a decrease in retention (46).
0.05	10	Solution containing 20 mM NaCl, 1 mM $CaCl_2$ and 1 mM $NaHCO_3$, and spiked with BPA.	8	A ceramic membrane, NF90 and NF270.	Retentions of 28%, 50% and 70% for NF270, NF90 and ceramic membrane respectively (37).

4 Methodology

4.1 Literature Guidance

To create an experimental plan, similar studies in literature were researched, to identify parameters to vary. The PROMETEO group's intention was to research two membranes, ideally comparing a membrane they had experience with to another type. The membranes available were NP010, NP030, NF270 and NF245. When researching literature, it was found of this selection only NF270 had been tested for BPA retention. Therefore, it was decided to use NP030 and NF270, as new information obtained from NP030 could be compared to NF270 data, both through experiments and literature. Literature searches helped shape the experimental plan, including the most relevant factors and BPA concentrations to test.

4.2 Chemicals

4.2.1 Bisphenol-A

BPA (97%, Aldrich) was dissolved in water to prepare solutions of BPA for nanofiltration. It was known BPA would dissolve easily in a mixture of water and acetonitrile, but there was a possibility acetonitrile could damage the membrane, as similar solvents have been seen to cause changes to polyamide membrane structures (54), so this was not feasible. Solutions were stored at 3 ^{o}C, to prevent degradation.

As the detection limit of the chromatography machine used to measure BPA concentration was 0.01 mg/L, the concentration of feed solutions proposed was 1 mg/L of BPA, to ensure precision to two figures in the retention results.

4.2.2 Glucose

Anhydrous glucose (99%, ITW Reagents) was used in some solutions.

4.2.3 Salts

NaCl (99.9%, LABKEM), sodium sulphate (Na_2SO_4) (98%, ITW Reagents) and magnesium sulphate ($MgSO_4$) (96%, ITW Reagents) were used for characterisation of the membranes. NaCl was also used to increase the ionic strength of some solutions. This allowed salt retentions to be calculated.

4.2.4 Sodium Hydroxide

Sodium hydroxide (98%, Panreac) was used to alter the pH of the feed solutions.

4.3 Membranes

The chosen membranes, NP030 and NF270, are compared in Table 4.1, and their data shown in Table 4.2. Figure 4.1 and Figure 4.2 show micrographs of their surfaces. When considering contact angle values, although NP030 is classed as one, it’s a relatively less hydrophilic membrane than NF270.

Table 4.1: Membrane Characteristics

Membrane	NP030	NF270
Manufacturer	Microdyn Nadir™	DuPont™
Material	PES with polypropylene backing (55).	Polyamide active layer with polysulfone support layer (56).
Attraction to Water	Hydrophilic (57)	Hydrophilic
Types of Pores and Surface	Mainly mesoporous (2-50 nm wide).	Mainly mesopores, although tighter than NP030.
MWCO (Da)	400 – 600.	200 – 400 (58)
Common Uses	Applicable to strong acidic and caustic environments, and the food and drink industry.	Water softening processes due to high efficacy in removing organic compounds.

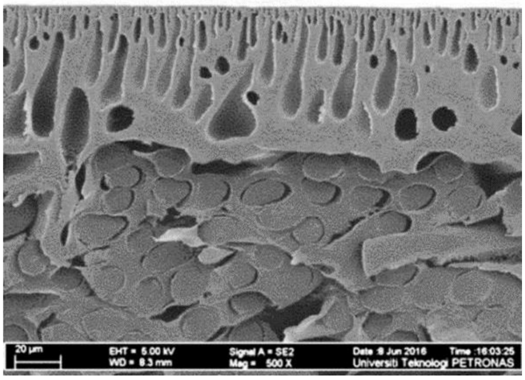


Figure 4.1: Micrograph of NP030 Surface (38)

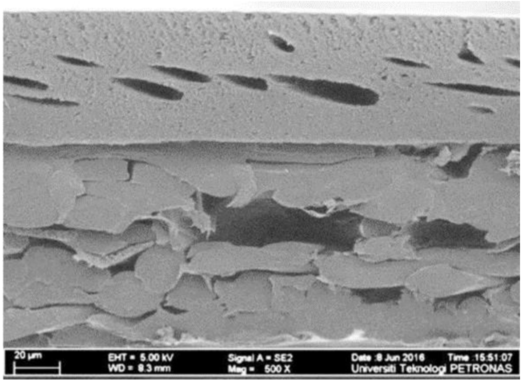


Figure 4.2: Micrograph of NF270 Surface (38)

Table 4.2: Membrane Data

Membrane	Maximum Temperature (°C)	Maximum Pressure (bar)	pH Range	Active Layer Thickness (nm) (59)	Average Pore Radius (nm) (56,60)	Contact Angle (°) (57)
NP030	95	40	0 – 14	N/A	0.93	58.0
NF270	45	41	3 – 10	21	0.41	15.9

4.4 Sterlitech Stirred Cell

A dead-end Sterlitech HP4750 stirred cell, made of 316 stainless steel, was used to carry out all experiments. The setup was per manufacturers recommendations, see Appendix 4.1. The cell capacity was 300 ml, with a hold-up volume of 1 ml and stir bar made of polytetrafluoroethylene. Procedure for assembly and operation can be found in Appendix 4.2. The cell was connected to a nitrogen tank to pressurise it, and pressure controlled using manual valves. Effective cell membrane area was 14.6 cm^2. The setup used is shown in Figure 4.3 and Figure 4.4

Figure 4.3: Experimental Setup

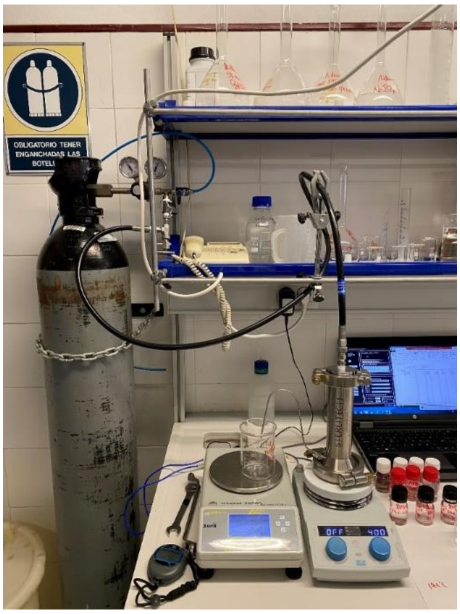


Figure 4.4: Experimental Setup

4.5 Conductivity and pH Measurements

The conductivity and pH of all samples were measured using a HACH HQ440d multi-meter. The probes were inserted into samples, left for a short period to acclimatise and then readings taken. A single reading of pH was taken, and three readings of conductivity were taken to calculate an average value.

4.6 Permeability and Characterisation Experiments

Initially membrane samples underwent pure water permeability (PWP) tests. Climatisation runs were carried out at 7 bar for a period of 30 minutes to allow the membrane to adjust to pressure. PWP experiments were carried out using water for 60-minute periods, to allow flux stabilisation, at pressures of 2, 4, 6, 8 and 9.5 bar.

The membranes were characterised with manufacturer's recommended salts in a similar fashion. For NP030, 5,000 mg/L Na_2SO_4 solution was used at 9.5 bar and for NF270, 2,000 mg/L $MgSO_4$ solution was used at 4.8 bar. To begin with a climatisation run was carried out, for 45 minutes, at an intermediate pressure. After this the characterisation run was carried out, for a minimum of 180 minutes, again to allow flux stabilisation. Permeate samples were collected every 15 minutes to measure conductivity, and a cumulative permeate sample was taken to measure the total accumulated permeate conductivity. This process was identical for both membranes. NP030 manufacturer data had been achieved at a pressure of 40 bar, but this was not feasible from the experimental setup, so the highest pressure possible was used instead. NF270 was also characterised with Na_2SO_4 for comparison to NP030, and with NaCl.

4.7 Experimental Runs

The study analysed the influence of pressure, pH, and ionic strength on BPA retention. Furthermore, glucose was added as a reference, as a well-known uncharged solute. The concentration of BPA and glucose was set at 1 mg/L. NaCl was used to alter the ionic strength of the solutions at two concentrations, 1,000 and 2,000 mg/L. Pressure was studied at two levels, 4 and 8 bar, and pH at two levels, 6 and 8. This resulted in 16 experimental runs being carried out for each membrane. The conditions of each experimental run are seen in Table 4.3. All experiments were carried out at room temperature, which varied between 17–21 ^{o}C. A stir speed of 400 rpm was used. Sodium hydroxide solution was added drop wise to feed solutions to alter their pH when required.

Table 4.3: Experimental Run Conditions

Run	Pressure (bar)	pH	BPA Concentration (mg/L)	Glucose Concentration (mg/L)	NaCl Concentration (mg/L)
1	4	6	1	0	0
2	8	6	1	0	0
3	4	6	1	1	0
4	8	6	1	1	0
5	4	6	1	1	1,000
6	8	6	1	1	1,000
7	4	6	1	1	2,000
8	8	6	1	1	2,000
9	4	8	1	0	0
10	8	8	1	0	0
11	4	8	1	1	0
12	8	8	1	1	0
13	4	8	1	1	1,000
14	8	8	1	1	1,000
15	4	8	1	1	2,000
16	8	8	1	1	2,000

When preparing experiments, the solution to be tested was added to the cell the day before, with the stirring bar active. Two experiments were conducted each day using the same feed composition but different pressures, thus after the first experiment the cell was emptied, rinsed with deionised water, and refilled with fresh feed solution. When beginning each experiment, the cell was pressurised to the required pressure. The first permeate was collected over a period of 60 minutes, to let the system stabilise, and the second permeate was collected over the following 15 minutes. The retentate was then collected.

One experiment was carried out with untreated wastewater doped with 1 mg/L BPA. The natural pH of the feed solution was 4.42, with a similar ionic strength to 1,000 mg/L NaCl solutions. The run was carried out at 8 bar with the NF270 membrane. This was the final experiment, as the wastewater would foul the membrane.

For experiments that were repeated at the end of the project, a new sample of NP030 membrane from the same sheet as the original membrane was used. Its permeability and characterisation experiments were carried out identically. In the following sections, the original sample will be referred to as the "1st NP030" and the new sample as the "2nd NP030". For experiments repeated with NF270, the same membrane sample was used so no additional characterisations were required.

4.8 Analysis Methods

High-performance liquid chromatography (HPLC) was used to analyse BPA concentration in feed, permeate, and retentate samples. To prevent large compounds (organic or inorganic) from damaging the column, the feed and retentate samples were filtered using a 0.2 µm PES membrane (RephiQuik syringe-filters).

A HPLC setup consisting of a low-pressure gradient HPLC pump (JASCO-PU-2089), photodiode array detector (JASCO-MD-2018), RHPLC autosampler (JASCO-AS-4150) and an interface box (JASCO-LC-Net II/ADC) was used. A 4.6 mm ID x 100 mm column (Kinetex XB-C18) was used, along with a UHPLC 4.6 mm ID security guard cartridge to protect the column from contamination. A mixture of 50% water - 50% acetonitrile was used as the mobile phase. The injection volume was 20 µL. The process of operation for the HPLC machine is described in Appendix 4.3.

Standard solutions of BPA in water ranging from 0.1-5 mg/L were prepared via dilution to allow a calibration curve to be created. BPA is known to have a retention time of approximately 2.5 minutes, which allowed the area under the chromatogram curve at this point to be calculated. Hence, a calibration curve of area vs concentration of standard samples was created, allowing the concentration of BPA samples to be calculated.

Glucose concentrations were calculated using the Anthrone method, which involved using a reagent called anthrone (9,10-dihydro-9-ozoanthracene), to react sulphuric acid with the carbohydrates in the samples (61). This gave the solutions a cyan colour which could then be measured using a spectrometer (HACH-DR-6000) at wavelength of 625 nm to determine their absorbance, which is proportional to the carbohydrates (i.e., glucose) concentration. Standard solutions of glucose from 0.1-2 mg/L were prepared by dissolving glucose in water and used to create a calibration curve.

4.9 Calculation Procedures

As in this study there was significant recovery, with two permeate samples collected, it was more precise to measure two retentions of BPA: the first permeate retention, R_1, Equation 4.1, and the second permeate retention, R_2, Equation 4.2. To calculate these, the permeate recovery, Y, was required, which is the ratio of permeate flow to feed flow, or for a discontinuous process the volume of permeate divided by the volume of the feed. C_{f0} is feed concentration, C_{p1} is first permeate concentration, C_{f2} is retentate concentration and C_{p2} is second permeate concentration.

$$R_1(\%) = \frac{-\ln\left(\frac{1-\frac{C_{p1}}{C_{f0}}Y_1}{1-Y_1}\right)}{\ln(1-Y_1)} \text{ x } 100 \qquad \text{Equation 4.1}$$

$$R_2(\%) = \frac{\ln\left(1-Y_2\left(1-\frac{C_{p2}}{C_{f2}}\right)\right)}{\ln(1-Y_2)} \text{ x } 100 \qquad \text{Equation 4.2}$$

BPA retentions were calculated using Equation 4.1 and 4.2. This second retention value is taken as the retention of BPA which is displayed in the results section.

At constant temperature, conductivity is proportional to concentration, so this allowed salt retentions to be calculated, where concentration ratios are replaced by conductivity ratios in the above equations.

4.10 DSPM

The DSPM was adapted for uncharged solutes. In this case the model was simplified as electrical-related terms could be negated. Parameters such as membrane pore radius and Stokes radii of solutes were sourced from literature, but membrane permeability was calculated experimentally. As the model was developed for uncharged molecules, it doesn’t include pH effects.

The BPA Stokes radius is highly influenced by ionic strength (62). It was taken to be 0.47 nm without the presence of NaCl, and 0.33 nm with NaCl. The lower radius when alongside NaCl is due to the ions causing BPA to adopt a more compact configuration and decrease in size. This model allowed predictions of the retention with and without the presence of NaCl to be calculated, and experimental results to be plotted against this.

The code used to predict the retention of BPA by NF270 using DSPM is shown in Appendix 4.4. This code was provided by José Marcial Gozálvez Zafrilla.

5 Results and Discussion

5.1 Membrane Flux and Characterisation

The pure water membrane fluxes after one hour of operation for each membrane are shown in Figure 5.1. Flux increased with pressure, which agrees with Darcy's Law. The PWP of each membrane was calculated, and compared with manufacturers values, Table 5.1. NF270 had a larger PWP which can be explained by its greater hydrophilic nature. Values for both membrane samples agree with manufacturer limits, which implied there was no membrane damage. NP030 membrane sample permeabilities differed by less than 10%, hence it was deemed acceptable to use results obtained from the second membrane.

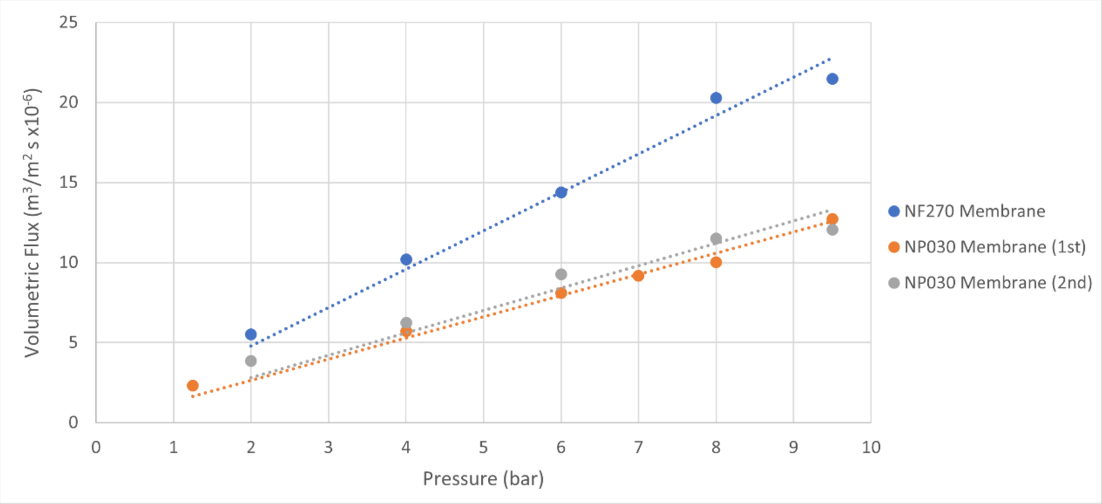


Figure 5.1: Pure Water Flux for NF270 and NP030

Table 5.1: Membrane PWP's

Membrane	**Experimental Pure Water Permeability (L/m² h bar)**	**Manufacturers Pure Water Permeability (L/m² h bar)**
NP030	4.76 (1st membrane), 5.04 (2nd membrane)	≥ 1 (55)
NF270	8.63	8.5 (63)

Table 5.2 shows the overall salt retention calculated using cumulative collected permeate.

Table 5.2: Overall Salt Retentions for NP030 and NF270 Membranes

Membranes	Final Na_2SO_4 Retention (%) (5,000 mg/L, 9.5 bar)	Final $MgSO_4$ Retention (%) (2,000 mg/L, 4.8 bar)	Final NaCl Retention (%) (2,000 mg/L, 8 bar)
NP030	33.9 (1st membrane), 47.8 (2nd membrane)	-	-
NF270	96.7	95.4	38.1

The NF270 results agree with manufacturer data (retention of $MgSO_4$ >97%), and are within the range of experimental results obtained from other authors (64). The NP030 results differ from manufacturers values (80-95% Na_2SO_4 retention) (55), this is assumed to be due to a lower pressure being used for characterisation. Nonetheless, retentions are still lower than expected for nanofiltration membranes. The first NP030 membrane sample is seen to have poorer retention than the second; this is the nature of using two different pieces of membrane from the same sheet, there is no guarantee of identical properties. The greater retention of Na_2SO_4 by NF270 compared to NP030 confirms NF270 has a smaller MWCO.

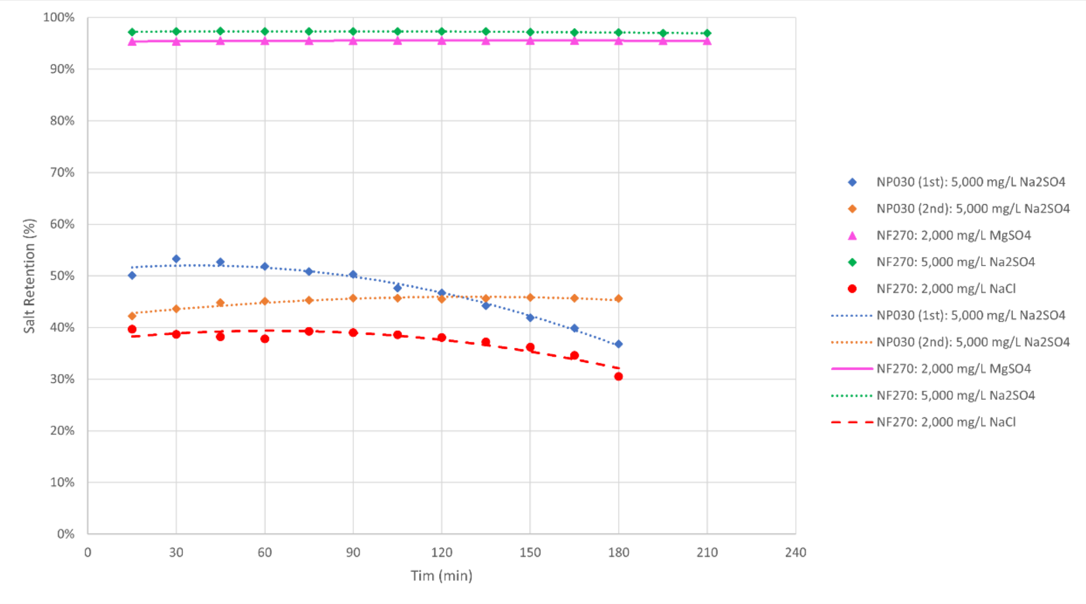


Figure 5.2: Retention of Characterisation Salts for NP030 and NF270 Membranes

Figure 5.2 displays the retention of salts calculated for each permeate collected during membrane characterisations, with 2nd order polynomic lines of best fit. As previously stated, retention was calculated according to Equation 4.1 and 4.2. Over time, the NF270 membrane maintained a constant retention of $MgSO_4$ and Na_2SO_4, but for NaCl retentions began to decrease after 90 minutes. This is likely due to the NaCl concentration increasing in the cell over time, due to the filtration process, to an extent that it began to cause a decrease in retention through concentration polarisation. For the second NP030 membrane sample, it's strange that retentions decrease near the end of the experiments; this was likely an anomalous result.

5.2 Flux Evolution in Time

Figure 5.3 shows the profile in time for the ratio of the flux to the maximum flux reached in selected experiments. The profile was the same for all experiments independent of the solution composition, operating pressure, and pH. This was observed for all other experiments (results not included).

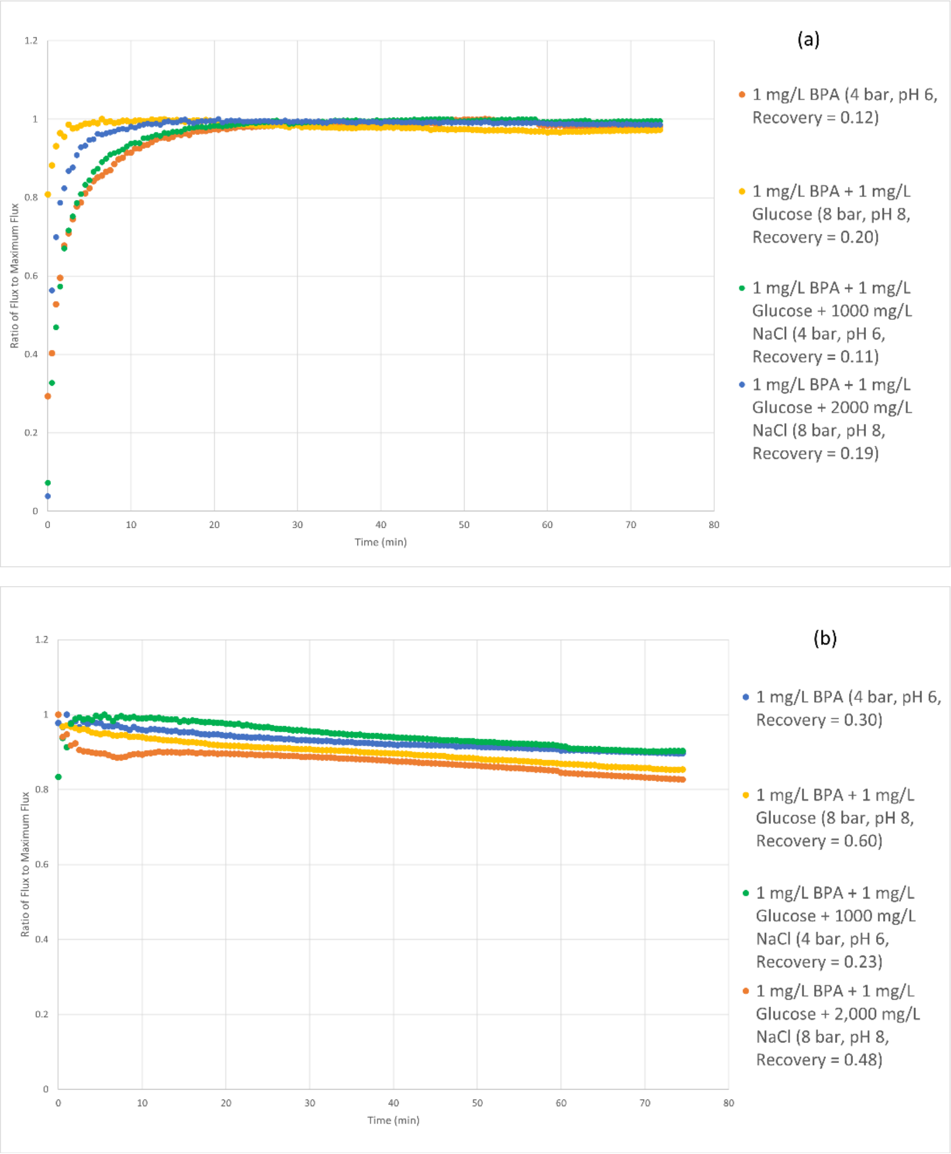


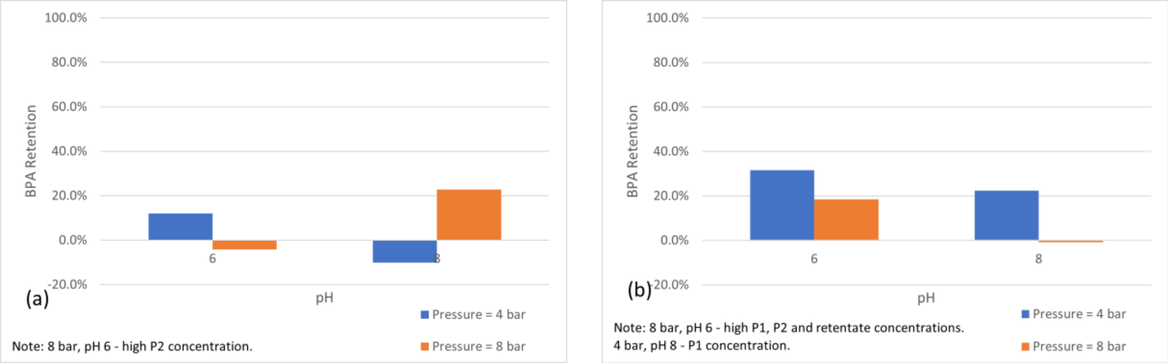
Figure 5.3: Ratio of Flux to Maximum Flux for Selected Experiments (a) NP030, (b) NF270

For the NF270 membrane, over time flux decreased which is expected. This is due to concentration of filtered solutes increasing in the retentate over time, thus osmotic pressure increased and the net driving force decreased, giving a decrease in flux, see Equation 3.2. It took longer for the NP030 membrane to acclimatise to the pressure, as initially it had lower flux values, but the same behaviour was observed.

5.3 NP030 Membrane

5.3.1 BPA Retention

As seen in Figure 5.4, BPA retention was below 22.8% for solutions of 1 mg/L BPA. Highest retention was seen at conditions of pH 8, 8 bar, which agrees with theories of higher pressure and higher pH giving greater retention (65). However, negative retentions were observed for two experiments, which doesn’t match with any expected trends. This is seen across different solutions for the NP030 membrane. Raw data and example calculations are shown in Appendix 5.1 and 5.2 respectively. All results are tabulated in Appendix 5.3, including repeated experiments. Anomalous results seen when measuring BPA concentration are stated in figures.



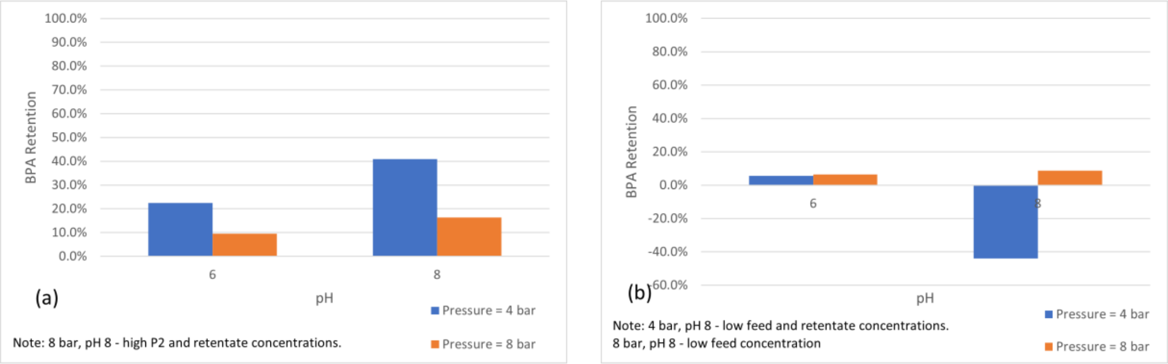
Note: 8 bar, pH 6 - high P2 concentration.

Note: 8 bar, pH 6 - high P1, P2 and retentate concentrations.
4 bar, pH 8 - P1 concentration.

Figure 5.4: BPA Retention for 1 mg/L BPA and (a) 0 mg/L Glucose, (b) 1 mg/L Glucose

For glucose inclusion, highest retention was seen at the lowest pressure and pH, which contradicts literature findings. It’s possible that experimental errors influence the other three experiments for this solution. For both pressures, at higher pH the retention of BPA decreased, ergo implying Donnan exclusion does not have any influence until the pH has increased beyond BPA’s pKa value of 9.6.

Figure 5.5 displays retentions of solutions including NaCl. For 1,000 mg/L NaCl solution, retention followed the expected pH trend, almost doubling when pH increased at a constant pressure of 4 bar, with a similar increase for the 8 bar experiments. This gave better results than for 1 mg/L BPA solution, which is surprising as at increased salt concentrations it’s expected retention should decrease due to the combination of BPA’s Stokes radius decreasing and NaCl causing pores to swell (43). Pressure increases led to retention decreases in both cases. The best BPA retention for NP030, 40.9%, was seen in these experiments. It’s possible here the main effect from NaCl was on the glucose or membrane interactions.



Note: 8 bar, pH 8 - high P2 and retentate concentrations.

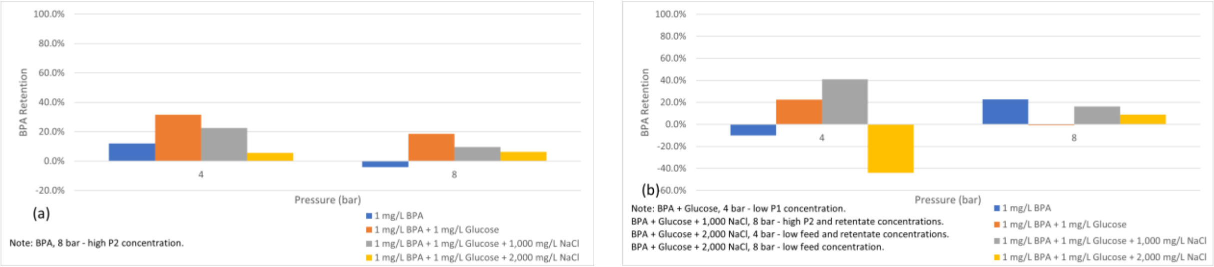
Note: 4 bar, pH 8 - low feed and retentate concentrations.
8 bar, pH 8 - low feed concentration

Figure 5.5: BPA Retention for 1 mg/L BPA, 1 mg/L Glucose and (a) 1,000 mg/L NaCl, (b) 2,000 mg/L NaCl

For the stronger 2,000 mg/L NaCl concentration solution, retentions at all conditions were poor, the highest being 8.8%. These closer matches literature predictions, as for higher NaCl concentration, salting out effect on BPA should be intensified. Increased pressure brought a very small retention increase at pH 6, and a large increase for pH 8. Due to its extremely poor result, the experiment at 4 bar, pH 8 was thought to have large experimental errors but due to time constraints repetition was not possible. In these experiments, pH had minimal impact on results.

Nanofiltration of chloride and nitrate ions in solutions has been seen to give negative retentions in literature (66,67). In both cases binary mixtures were being assessed, and at high salt concentrations other ions in solution were attracted to the membrane due to their charge. This shielded the membrane's charge and allowed chloride and nitrate ions to pass through the pores. This is not as applicable in this study as BPA is a neutral molecule but gives an insight into negative retention possibilities.

5.3.2 Effect of Pressure



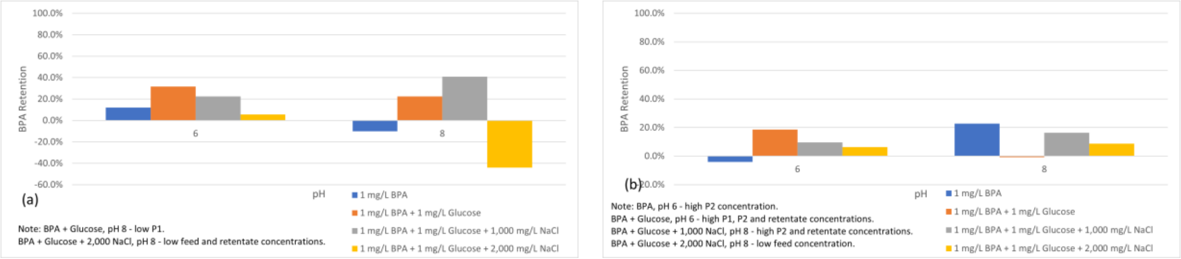
Note: BPA, 8 bar - high P2 concentration.

Note: BPA + Glucose, 4 bar - low P1 concentration.
BPA + Glucose + 1,000 NaCl, 8 bar - high P2 and retentate concentrations.
BPA + Glucose + 2,000 NaCl, 4 bar - low feed and retentate concentrations.
BPA + Glucose + 2,000 NaCl, 8 bar - low feed concentration.

Figure 5.6: BPA Retentions for Solution of (a) pH 6, (b) pH 8

From Figure 5.6, increasing pressure from 4 bar to 8 bar was generally found to give a decrease in BPA retention. Out of the eight comparable conditions, BPA retention only increased in three. From this it can be drawn that despite nanofiltration being a pressure driven process, when testing retention of molecules smaller than the MWCO of the membrane, it's preferable to operate at lower pressures.

5.3.3 Effect of pH



Note: BPA + Glucose, pH 8 - low P1.
BPA + Glucose + 2,000 NaCl, pH 8 - low feed and retentate concentrations.

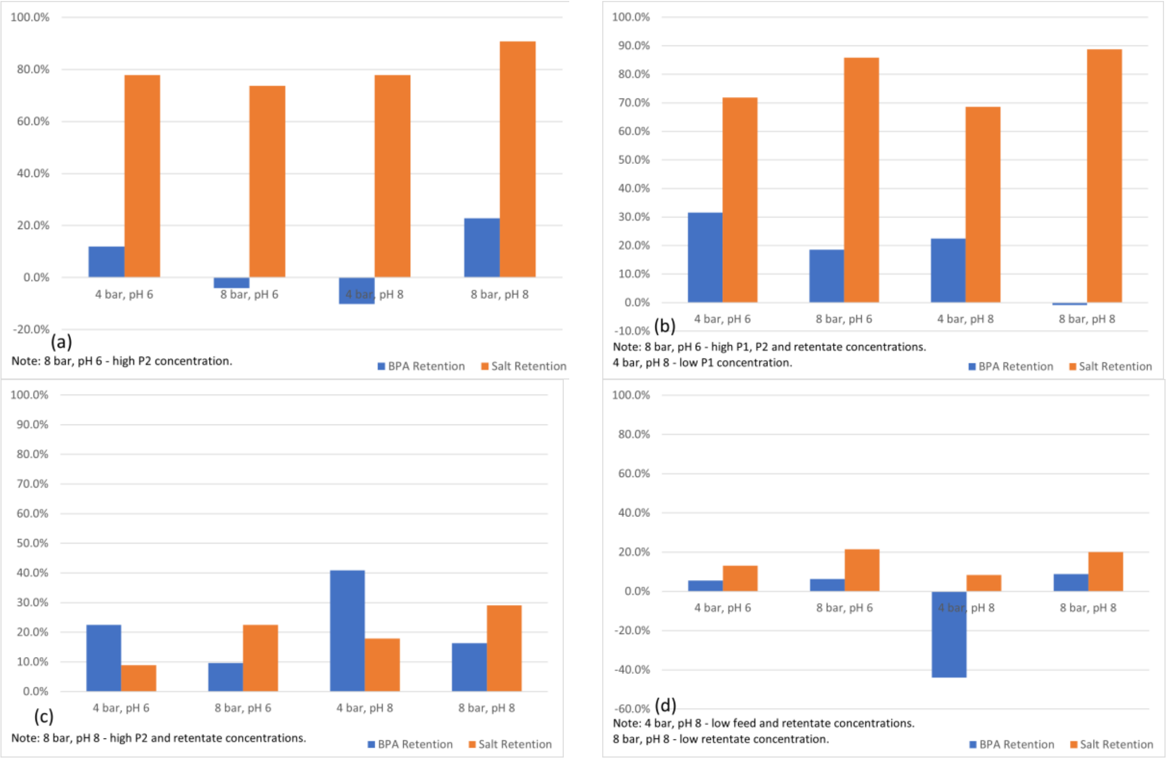
Note: BPA, pH 6 - high P2 concentration.
BPA + Glucose, pH 6 - high P1, P2 and retentate concentrations.
BPA + Glucose + 1,000 NaCl, pH 8 - high P2 and retentate concentrations.
BPA + Glucose + 2,000 NaCl, pH 8 - low feed concentration.

Figure 5.7: BPA Retentions for Pressure (a) 4 bar, (b) 8 bar

Results in Figure 5.7 show no discernible trends. For 8 bar, an increase in retention was seen in all experiments when pH increased except for the BPA and glucose solution. Meanwhile at 4 bar, three of the four comparisons showed that retention decreased as pH increased, in contrast to the higher-pressure experiments. Retentions are so poor for NP030, and results so varied that no solid conclusions can be drawn. It may be hypothesised that when operating at higher pressures, higher pH leads to more effective retention, but at lower pressures it's preferable to work with lower pH.

5.3.4 Effect of Glucose and NaCl

Originally it had been planned to analyse relevant samples for their glucose content to determine its retention in comparison to BPA. Due to time restraints this wasn't possible, however it should be investigated in future. From Figure 5.8, it could be drawn that the presence of glucose did increase the retention of BPA for three of the conditions, but any effect was small. This was possibly due to adsorption between BPA and glucose molecules, although repetition of these experiments is required to confirm this. For the experiments that did not contain any NaCl, the salt retentions are based on salts that were present in the water used to make solutions. Note that adjusting pH using NaOH was seen to slightly increase the conductivity of the original feed solutions as this increased the quantity of ions in solution.



Note: 8 bar, pH 6 - high P2 concentration.

Note: 8 bar, pH 6 - high P1, P2 and retentate concentrations.
4 bar, pH 8 - low P1 concentration.

Note: 8 bar, pH 8 - high P2 and retentate concentrations.

Note: 4 bar, pH 8 - low feed and retentate concentrations.
8 bar, pH 8 - low retentate concentration.

Figure 5.8: BPA and Salt Retention for 1 mg/L BPA and (a) 0 mg/L Glucose, 0 mg/L NaCl, (b)1 mg/L Glucose, 0 mg/L NaCl, (c) 1 mg/L Glucose, 1,000 mg/L NaCl, (d) 1 mg/L Glucose, 2,000 mg/L NaCl

Focusing on only NaCl results, it's clear increasing NaCl concentration from 1,000 to 2,000 mg/L led to a decrease in BPA retention. Again, this is likely due to the salting out effect affecting BPA and pore sizes. Additionally, at 1,000 mg/L NaCl, retention is greater than for BPA only solution, which correlates with another study (42).

At constant pH it's observed an increase in pressure gave an increase in NaCl retention which proves the relationship between increased pressure giving increased retention (68). The retention of NaCl being around 20-30% corresponds with literature data for NP030, where it has been reported in the pressure range of 5-10 bar NaCl is retained at approximately 25% (60).

5.3.5 DSPM for NP030

Using an average pore radius for NP030, the DSPM was applied to predict BPA retention and compare against experimental results, see Figure 5.9, although negative retentions were not included. DSPM assumes pore radius is proportional to the square root of permeability, so this this allowed confidence bounds to be applied to the model, with the assumption membrane permeability varies by +/-15%.

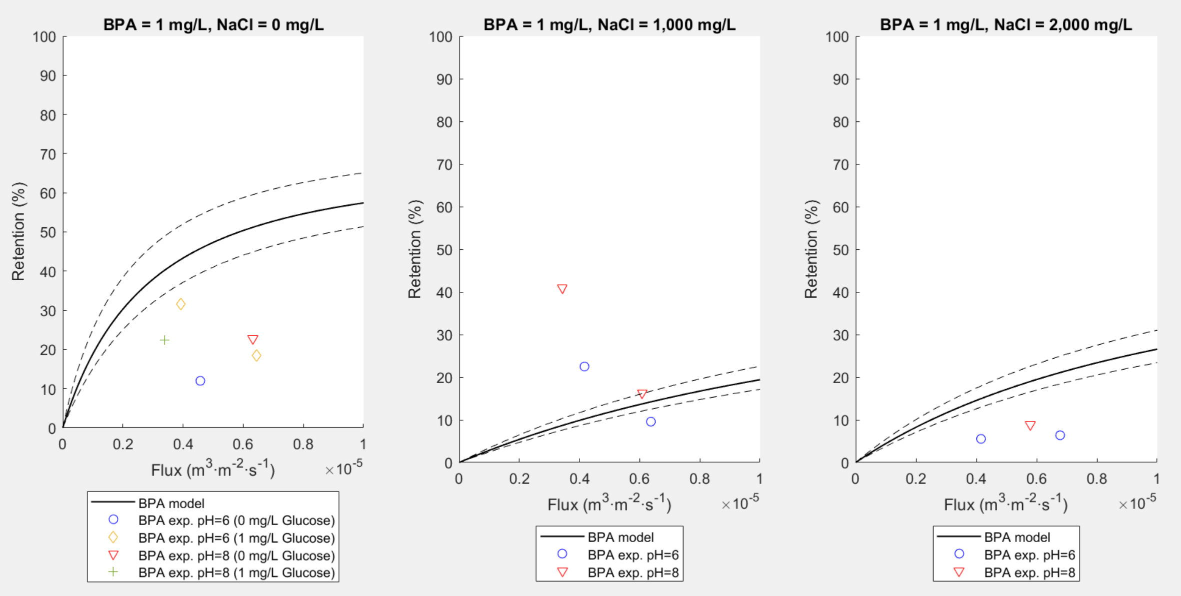


Figure 5.9: DSPM for NP030

All experimental results for 0 and 2,000 mg/L NaCl are below the predicted retention values based on NP030's pore size. From the predicted model it was clear that BPA should be more readily retained at minimal salt concentrations, but results at 0 mg/L of NaCl are poor, where retentions decrease with increased flux. Predictions for 1,000 mg/L NaCl are the most accurate.

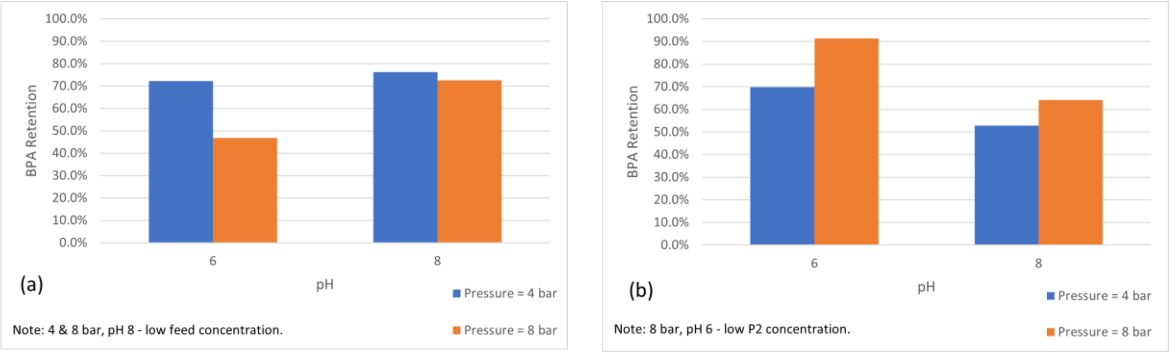
This model predicts a general decrease in BPA retention with increase in ionic strength and indicates BPA retentions in general for NP030 are low. This must be noted if considering its use for industrial applications, as additional or complimentary treatments would most likely be required.

5.4 NF270 Membrane

5.4.1 BPA Retention

For 1 mg/L BPA solution, Figure 5.10, improved retentions of BPA were observed using NF270, and this is in line with expectations, as NF270 is a tighter membrane. Increasing pH is seen to have increased retention, and conversely increased pressure gave a decrease in retention. The result for 8 bar, pH 6 was unusually low, possibly due to analytical errors.

In literature NF270 has been reported to give BPA retention of 80% for feed concentration of 50 mg/L, at 10 bar, pH 6 (7). Comparing the 8 bar, pH 6 experiment where 46.8% retention was observed, these results differ remarkably; the lower retention observed here could agree with the lower pressure used, but the literature study did use high feed concentration. Pressure should be seen to increase retention due to increasing diffusive effects, see DSPM.

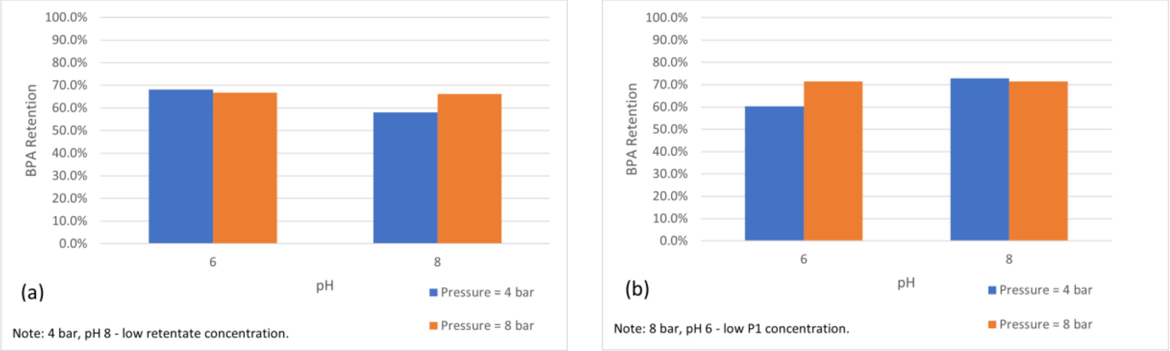


Note: 4 & 8 bar, pH 8 - low feed concentration.

Note: 8 bar, pH 6 - low P2 concentration.

Figure 5.10: BPA Retention for 1 mg/L BPA and (a) 0 mg/L Glucose, (b) 1 mg/L Glucose

For solutions including glucose, the highest BPA retention for this membrane was observed, 91.4%. These results contrast with those of the pure BPA solution; for pressure increase, retention increased, and increased pH gave decreased retentions. While the pressure trend matches literature, the pH trend was reminiscent of that seen for NP030, further emphasising Donnan exclusion is not effective below pH 9.6.



Note: 4 bar, pH 8 - low retentate concentration.

Note: 8 bar, pH 6 - low P1 concentration.

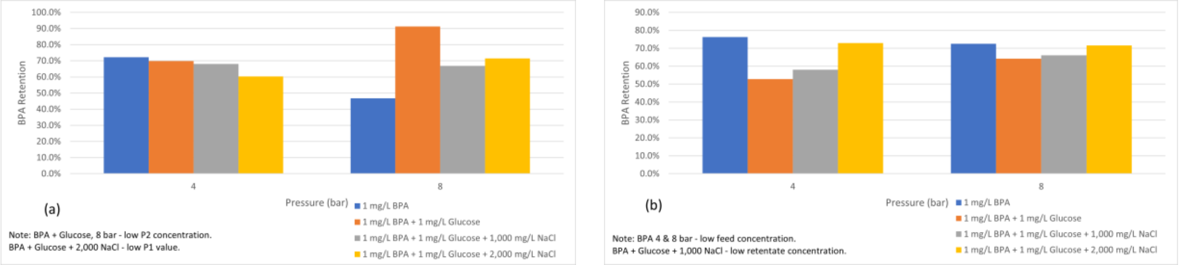
Figure 5.11: BPA Retention for 1 mg/L BPA, 1 mg/L Glucose and (a) 1,000 mg/L NaCl, (b) 2,000 mg/L NaCl

Figure 5.11 shows at concentrations of 1,000 mg/L, NaCl seemed to have little effect on BPA retention. Compared to the pure BPA solution, it gave equal or poorer retentions for all conditions. For pH 6, pressure increase gave insignificant change in retention, and at pH 8 it gave a minor increase. Equally, changing pH only gave small changes; for 4 bar, retention was lower at higher pH, and for 8 bar, results were indistinguishable.

At 2,000 mg/L of NaCl, most retentions were almost identical: only the 4 bar, pH 6 experiment differed, with 60% retention. At pH 6 increasing pressure gave a 10% increase in retention, whereas at pH 8 it gave a 1.4% decrease. Increasing pH from 6 to 8 gave an increase in retention at 4 bar, but no change was found at 8 bar.

5.4.2 Effect of Pressure

At pH 6, Figure 5.12, results are mixed between pressures. For 1 mg/L BPA solution, molecules were retained more effectively at lower pressure, whereas the other solutions show equal or better retention at higher pressure. For pH 8, the 1 mg/L BPA solution once again gave higher retention at lower pressure, and for the other solutions results were varied. When considering both pH levels, it can be concluded that for a solution of only BPA, lower pressure is preferable to achieve the best retention, but when other components are present higher pressures are required. This may be related to the molecular interactions that these additional components cause within the solution and with the membrane surface.

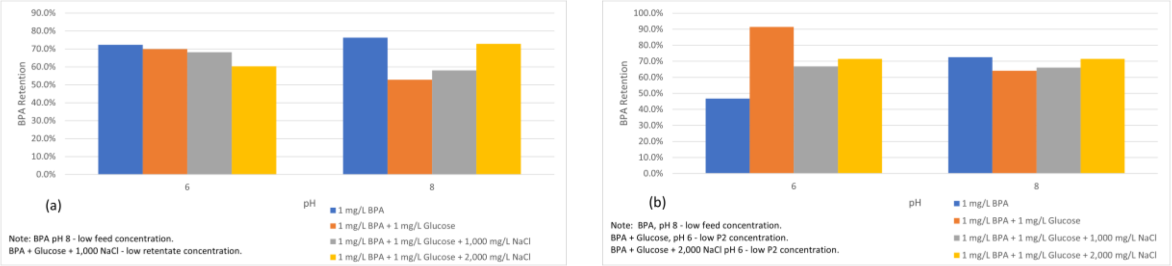


Note: BPA + Glucose, 8 bar - low P2 concentration.
BPA + Glucose + 2,000 NaCl - low P1 value.

Note: BPA 4 & 8 bar - low feed concentration.
BPA + Glucose + 1,000 NaCl - low retentate concentration.

Figure 5.12: BPA Retention for Solution of (a) pH 6, (b) pH 8

5.4.3 Effect of pH



Note: BPA pH 8 - low feed concentration.
BPA + Glucose + 1,000 NaCl - low retentate concentration.

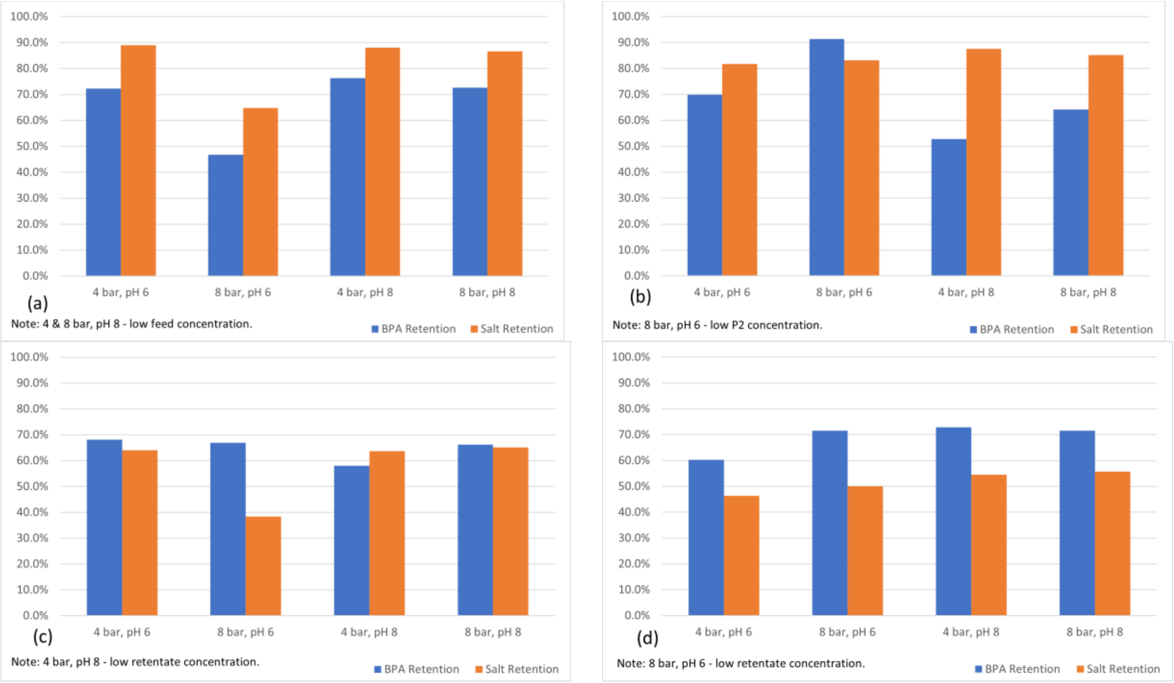
Note: BPA, pH 8 - low feed concentration.
BPA + Glucose, pH 6 - low P2 concentration.
BPA + Glucose + 2,000 NaCl pH 6 - low P2 concentration.

Figure 5.13: BPA Retention for Pressure of (a) 4 bar, (b) 8 bar

Once again, the effect of pH at 4 bar was mixed, see Figure 5.13. For pH 6, the retention of BPA decreased as components were added to the solution. At pH 8 for this pressure, the best retention occurred with pure BPA solution. For 8 bar experiments there was no clear trend in the data. At pH 6 the highest retention was seen with the mixture of BPA and glucose, and for pH 8 it was with pure BPA solution.

Donnan exclusion for BPA molecules using NF270 has been proven by changing pH from 6 to 11, which increased retention of a 0.5 mg/L BPA solution from 40% to 90% (42). Therefore, it seems clear that the Donnan exclusion principle does not affect BPA retention till pH is greater than the compound's pKa value, i.e., when the compound is ionised.

5.4.4 Effect of Glucose and NaCl



Note: 4 & 8 bar, pH 8 - low feed concentration.

Note: 8 bar, pH 6 - low P2 concentration.

Note: 4 bar, pH 8 - low retentate concentration.

Note: 8 bar, pH 6 - low retentate concentration.

Figure 5.14: BPA and Salt Retention for 1 mg/L BPA and (a) 0 mg/L Glucose, 0 mg/L NaCl, (b)1 mg/L Glucose, 0 mg/L NaCl, (c) 1 mg/L Glucose, 1,000 mg/L NaCl, (d) 1 mg/L Glucose, 2,000 mg/L NaCl

Figure 5.14 shows the comparison of BPA and salt retentions. For all but one of the eight NaCl experiments, BPA retention was greater than NaCl retention. At the higher salt concentration, NaCl was generally more poorly retained by NF270. However, comparing between the two NaCl concentrations shows that BPA retention values were greater at the higher ionic strength. This contradicts literature knowledge such as the salting out effect, or the Stokes radius of BPA decreasing, but adds weight to the theory that interactions between salt, other organics and the membrane surface affects retention. Comparison with NF270 literature shows 29% NaCl retention from a solution of 5,000 mg/L NaCl, therefore confirming that NaCl retention does decrease with increasing NaCl concentration (69).

Previously NF270 has been tested for BPA retention using electrolyte solutions including NaCl (at concentrations of approximately 1,000 mg/L) and spiked with BPA, at a pH of 8 (37,51). These have been compared with experiments at pH 8 and shown in Figure 5.15. This analysis shows no clear trend, although may be skewed by the large concentration used for the 10 bar experiment. If this result is discounted, then it appears increasing pressure at low concentrations of BPA brings retention to a maximum value before it begins to decrease. This implies that there is an optimal pressure somewhere between 4 and 13 bar for BPA retention in the presence of NaCl.

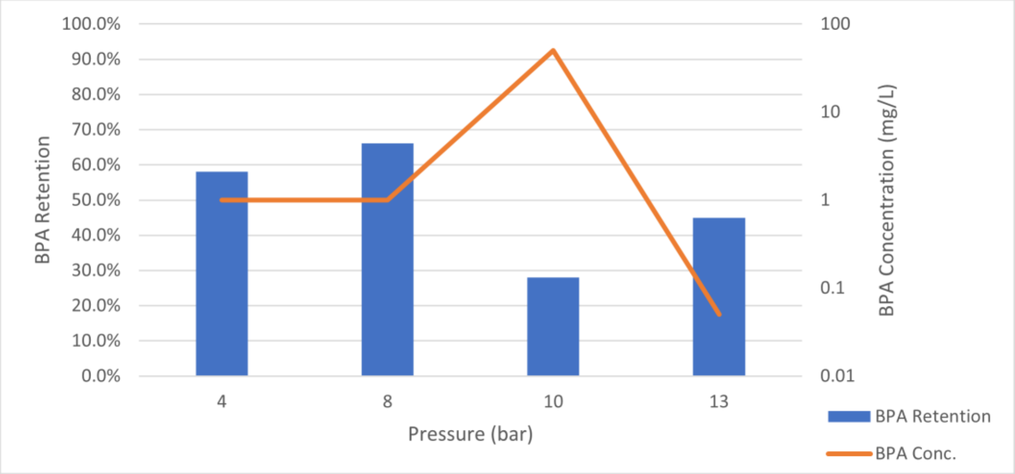


Figure 5.15: Comparison of BPA Retentions for NF270 with Literature (1,000 mg/L NaCl)

Conversely, other research has suggested ionic strength causes no change to BPA retention (42). At approximately 2,900 mg/L NaCl, for a 0.5 mg/L BPA solution, minimal difference in retention was observed. This may also be a valid theory, as the retentions in this report are not always consistent, hence the differences may be due to experimental errors and in fact NaCl presence had no impact.

Glucose retention was measured for a single NF270 experiment (4 bar, pH 6, 2,000 mg/L NaCl solution), and found to be 55.8% for the second permeate, with BPA retention being 60.3%. Thus, glucose had a marginally smaller retention which matched with expectations, as it has a slightly smaller Stokes radius, 0.39 nm (70). This reinforces the theory that size exclusion is the principal mechanism for nanofiltration retention.

5.4.5 DSPM for NF270

The DSPM was applied to the NF270 membrane, Figure 5.16, using average pore radius data, again including confidence bounds with the same assumptions as NP030’s DSPM.

Results for both NaCl concentrations being above predicted values was unanticipated and gives added weight to the theory that salts can interact with the membrane and other feed components, creating conditions that increase retention. Increased pressure shows greater retention for some results but not all, which implies more research is necessary in this area.

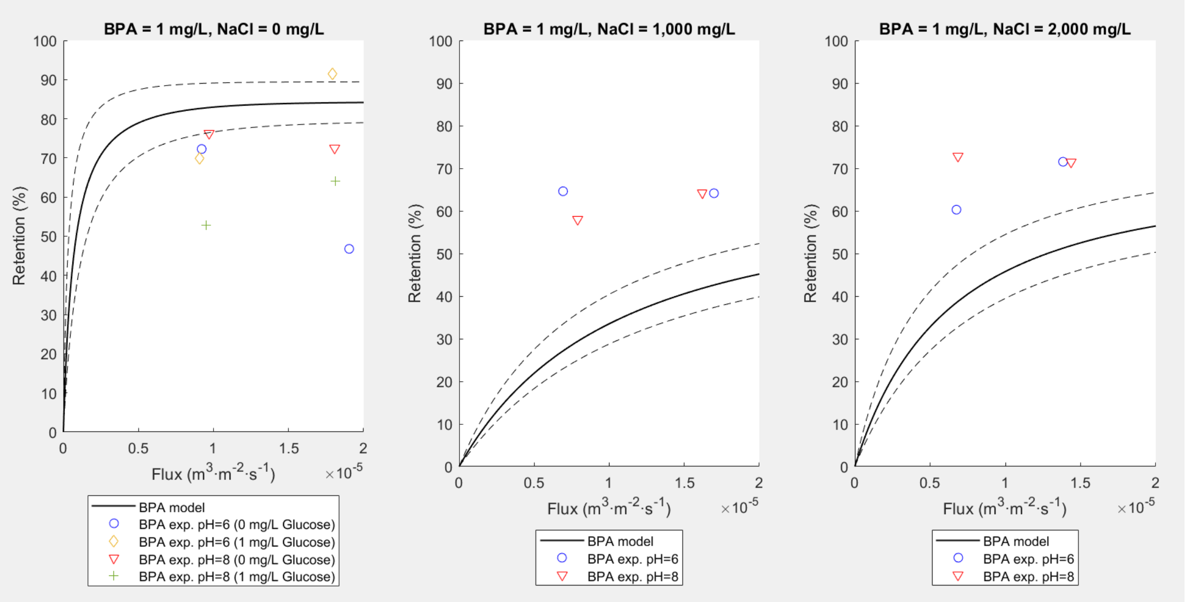


Figure 5.16: DSPM for NF270

Although all results do not match the prediction accurately, it must be noted there will always be differences in pore sizes for membrane samples from different sheets.

5.5 Wastewater Experiment

The results of the final NF270 experiment with wastewater is shown in Figure 5.17, including comparison with the two 1 mg/L BPA, 8 bar experiments for NF270.

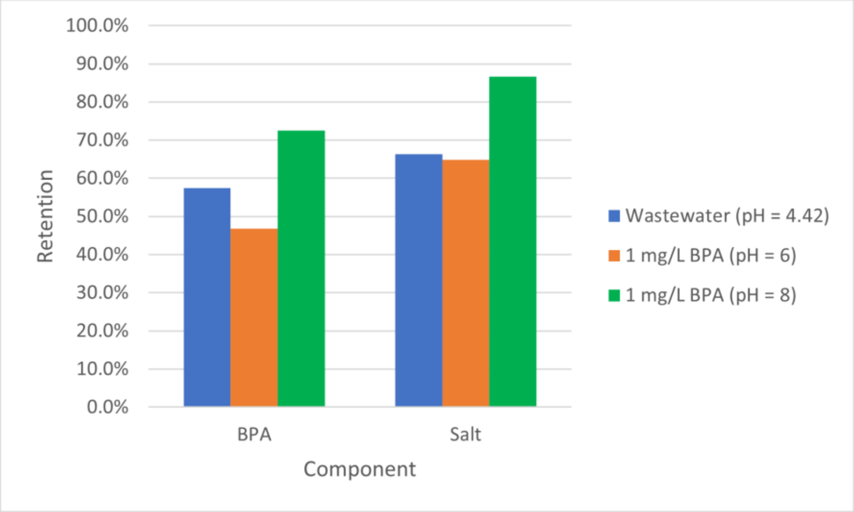


Figure 5.17: NF270 Wastewater Experiment Results

For real wastewater, better retention was obtained than for the pH 6 solution, but not the pH 8 solution. For this small sample size, it is unclear if pH does have an impact on retention of BPA as a neutral molecule.

The membrane flux for the wastewater sample was 1.63x10^{-5} m^3/m^{2}s, compared to 1.82x10^{-5} m^3/m^{2}s and 1.96x10^{-5} m^3/m^{2}s for the pH 6 and 8 bar experiments respectively. This could have been caused by components in the wastewater adsorbing to the membrane, causing permeability to decrease. This was expected, as there are many dissolved substances in untreated wastewater, which could block pores and cause changes to membrane active layer. The exact composition of the wastewater was unknown, but the ionic strength was alike that seen for 1,000 mg/L NaCl solutions. If a higher pressure had been tested, a flux closer to that of the pH 8 experiment could perhaps have been reached, possibly giving similar retention.

Despite this positive result, more thorough experiments are required to draw solid conclusions regarding NF270 performance with real wastewater. In future it would be essential to analyse wastewater feeds to understand their composition, and thus what factors would be influencing retention mechanisms. Nonetheless, NF270 could be used for BPA removal in these circumstances, depending on feed conditions, and intended permeate use.

5.6 Membrane Comparison

Figure 5.18 shows a comparison of all BPA retentions for all experiments conducted, and observed trends are stated in Table 5.3. It's clear to see NF270 performed better for BPA retention at every condition assessed. This is believed to be due to the difference in MWCO sizes of the membranes and therefore reinforces the theory that for uncharged molecules, size exclusion is the principal mechanism for molecular retention.

Table 5.3: Retention Results Comparison

Membrane	NP030	NF270
Pressure Effect	Increase in pressure gave decrease in retention.	Increase in pressure gave increase in retention, expect for BPA only experiments, which had better retention at lower pressure.
pH Effect	No evident trend in the range.	No evident trend in the range.
Glucose Effect	Inclusion possibly caused increase in retention, but further investigation required.	Generally decreased retention, but further investigation required.
Ionic Strength Effect	Lower ionic strength found to give best retention values, compared to both BPA only and higher ionic strength experiments. Increasing ionic strength to higher value gave decrease in retention.	Higher ionic strength experiments gave better retention than lower strength, and similar results to BPA only experiments
Salt and Glucose Effect	Possibly increased retention at lower ionic strength, but further investigation required.	Possibly increased retention, but further investigation required.

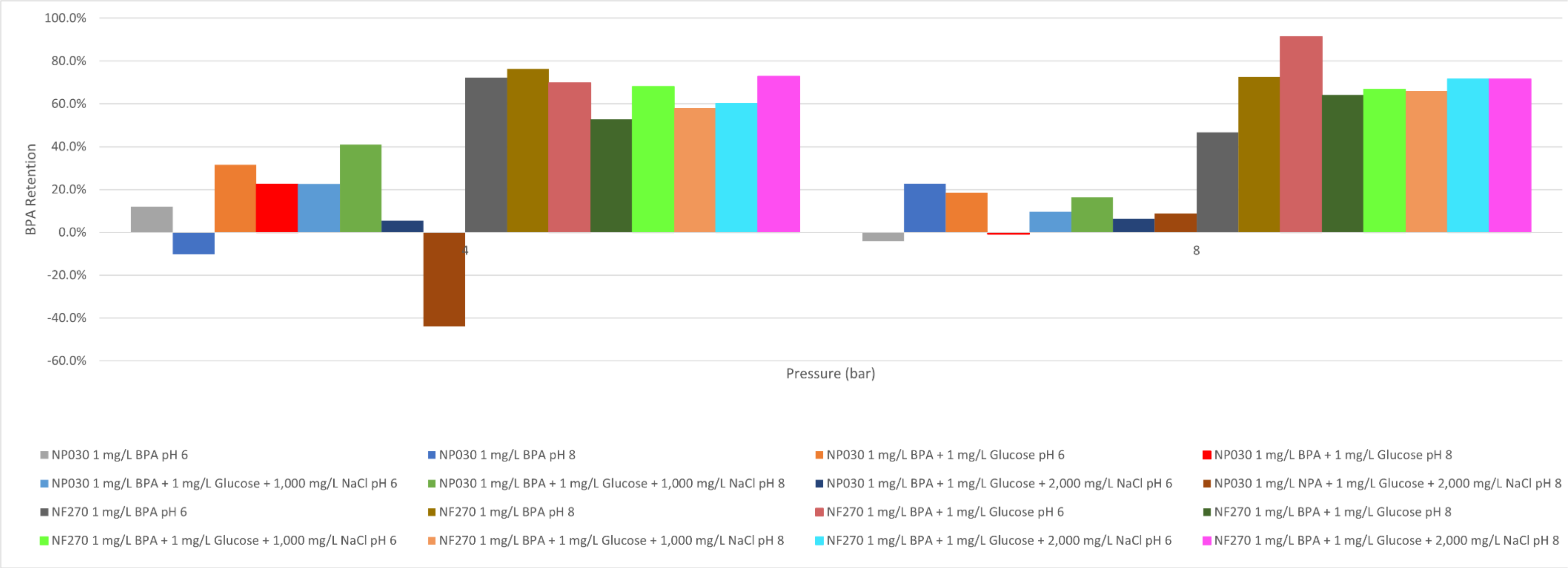


Figure 5.18: Retention of BPA for All Experiments

5.7 Issues Faced

Although soluble in water, it was found challenging to dissolve BPA, and as such the feed solutions when measured were found to have lower BPA concentrations than intended, varying between 0.1-1 mg/L. Similar issues were faced when trying to attain a calibration curve for HPLC analysis; a dilution method was used with 50% water-50% acetonitrile to prepare standard samples but again they did not correlate to the expected concentrations. Instead, a recent BPA calibration curve for the same equipment was obtained from the PROMETEO group and used to calculate concentrations. Future studies should strive to find more successful methods of solution preparation; research into a solvent that would dissolve BPA while not damaging membrane surfaces should be undertaken. This would in turn give more consistent feed solution concentrations, and thus more reliable comparisons between results.

Originally it had been planned to analyse each feed, permeate and retentate sample to determine their glucose content. Unfortunately, due to time constraints this was not achieved, hence full comparison of BPA and glucose retentions couldn't be carried out. It was also intended to repeat experiments where BPA retentions were poor or extremely different from what was predicted based on literature, but again due to time limitations this was not possible.

Due to the nature of the equipment, the holdup volume in the Sterlitech cell meant mass balances were not able to be verified for each experiment. This also proved an issue when beginning new experiments, as the initial 1 ml of permeate would be from the previous solution and not the solution being tested, thus could contaminate the new samples. To circumvent this, the first 1.5 g of permeate measured on the electronic balance for each run was discarded.

Experimental errors were expected to exist in the results, due to things such as small quantities of collected permeate not being weighed when switching beakers for first and second permeates and having to use different sized measuring flasks to measure permeate and retentate volumes.

5.8 Areas for Future Work and Consideration

If given more time, further repetition of experiments could have been carried out to verify if poor retentions were indeed due to conditions or in fact were due to experimental errors. Experiments which provided ‘good’ results could likewise be repeated to ensure reliability. The characterisation of NP030 with $MgSO_4$ and NaCl could be carried out to allow for a more detailed comparison with NF270. As the performance of nanofiltration membranes has significant variations, the study must also be extended to other membranes.

Regarding experimental conditions, pH and concentration could be varied further to investigate their influence. As the BPA molecules only turn negatively charged at pH of 9.6 or above, experiments for NP030 could be carried out at pH 11 to test if this improves retention through Donnan exclusion. This could then be compared to similar NF270 results in literature (42). Similarly, lower concentrations of BPA could be tested, as this would give more reliable results that are comparable to WWTPs (52). However, at PROMETEO, this would be difficult due to the lower detection limit of BPA by the HPLC equipment.

Fouling of the NP030 membrane could be tested using organic matter, to test if this improves retention as seen for other membranes (44). It should be noted that research would need to be conducted to find a suitable organic compound to use, so that the membrane is not damaged in the process.

Future work outside of this study’s scope should aspire to examine the impact real NOM concentration has on retention at varying conditions (pH and pressure). This could be expanded to test real NOM and salt effects on the membrane to make more informed conclusions on the matter.

Optimisation of conditions for BPA removal could now be carried out for NF270, with the knowledge gathered in this report. This could lead to more experiments being carried out with real wastewater for NF270 to test if the positive retention obtained here is consistently repeatable. It would also be beneficial to use wastewater from different sources to achieve results from a wide range of compositions, which in turn would give greater understanding of retention mechanisms and allow predictions of the membrane’s applicability to WWTPs processes.

The membranes used were retained, for the purpose of carrying out scanning electron microscopy on them to see how the experiments altered their surface. This would be very interesting for the NF270 membrane to see if the wastewater caused heavy fouling to its upper layer.

The research undertaken in this study will be continued after the completion of this report, with the nanofiltration of other microplastics, 4-nonylphenol and dimethyl terephthalate, being tested in the same experimental setup with Synder membranes.

6 Conclusion

This report has provided a detailed assessment of BPA removal using nanofiltration membranes, including both theoretical and experimental information. A literature study was performed to gather data on previous studies of BPA nanofiltration, and types of retention mechanisms. Size exclusion, Donnan exclusion, and solution ionic strength were perceived to be the dominant principles for uncharged molecules like BPA.

This process resulted in selection of two membranes, NP030 and NF270, to be tested experimentally for retention of 1 mg/L BPA solutions. Experimental factors were varied as followed: pressure (4 and 8 bar), pH (6 and 8), solution ionic strength (0, 1,000, and 2,000 mg/L) and glucose concentration (0 and 1 mg/L). Identical experiments were performed for each membrane to ensure reliable accurate comparisons could be made. This gave a wide scope for analysis, and additionally DSPM was applied to both membranes to give supplementary results.

For NP030, BPA retentions across each condition were found to be poor, with only a single experiment giving retention greater than 25%, indicating this membrane is unlikely to be applicable for BPA removal operations. The trend from literature of increased pressure leading to increased retention was not witnessed; however higher ionic strength causing poorer retention was observed. Overall retention was varied, but low for each solution tested.

In contrast, NF270 gave BPA retentions in a range of 46.8–91.4% across assessed solutions. Generally, pressure increase was seen to raise retention values, and high ionic strength surprisingly increased retention, although it's hypothesised this is related to its interactions with glucose. In both membranes, increased pH was seen to have no obvious effect on retention, confirming that Donnan exclusion is not influential below BPA's pKa value of 9.6. Due to time restraints, glucose retentions were not measured.

A final experiment was carried out using NF270 and a real wastewater sample doped with BPA, with retention seen to be 57.5%. This gave greater retention than a comparable experiment at pH 6 but was lower than the same experiment at pH 8. Nevertheless, it is an encouraging result for future work.

To conclude, NF270 is found to be a more effective membrane than NP030 for retaining BPA from solutions doped with BPA, and solution mixtures of BPA, glucose and NaCl. It also gave impressive results from a real wastewater sample. As such, it is seen to be a more feasible membrane for use in industrial WWTPs for BPA removal, although further research is still necessary.

7 Reflection and Review

In the undertaking of this project, I have enhanced my skillset in research as a fledging academic and nurtured my idea of self. This should enhance my performance in my doctoral studies after the completion of my degree. I have improved my confidence and ability to manage workloads efficiently throughout the project. My ownership of tasks and deadlines ensured that progress was achieved and presented in a concise way, during the study's duration.

Working on this project I accultured to the environment of the research group, by cultivating relationships established in the procurement and sharing of knowledge. After learning myself, I spent time showing fellow researchers the operation and analysis procedures required for the equipment I used, so that my research may be continued even after the submission of my report, while they introduced me to assays such as the Anthrone method. The significance of teamwork and communication brought a clarity of collective thinking following through to actions, which not only helped me overcome challenges in my report but also aided in other studies.

The knowledge from previous modules such as Particle Technology, Advanced Separations and Problem Solving, and Environmental Technology had provided a groundwork of knowledge which I was then able to build upon as my research and interpretation of the project advanced. Leaning more about the subject of micropollutants was very intriguing and I feel has enhanced my appreciation of the need for a circular economy to become the new normal, as having more consideration for the design and long-term fate of our products is the only way we shall avoid further challenges such as BPA pollution in society. The project principles also related to my upcoming PhD topic, which involves carbon capture using adsorbent materials, hence it was interesting to see concepts of environmental engineering applied in a similar situation.

With regards to the learning outcomes I set myself at the inception of the project, I feel I accomplished them to a satisfying standard. The opportunity to carry out laboratory work in a research group was important to me as I will be continuing my journey in academia on completion of my degree, by undertaking an experimentally focused PhD. This project therefore provided the bridge to transition from my master's degree to the next stage of my career and helped encourage a mindset of open-ended learning rather than working towards a known solution. The practical experiences I have obtained not only enhanced my understanding of the subject matter, but my enjoyment of the project, which in turn spurred me to deliver an impactful and quantified report. Similarly, it has refreshed and developed my lab skills, which shall be beneficial in the coming years.

I enjoyed the experience of a different city, and flatmates who briefly shared a common goal of attainment and purpose. I feel integrated into the Spanish way of life and its combination of various work and social aspects in balance, which I believe has been a valuable life experience.

8 Budget

To calculate the economic cost of carrying out this project, a budget has been prepared. This takes into account the cost of research activities, equipment, consumables, indirect costs and tax (VAT). It does not account for any personnel or work outside of UPV.

8.1 Research Activity Costs

These costs cover the work carried out by personnel on the project, and the analysis of the results, but not including any materials or chemicals used in the process. They are shown in Table 8.1.

Table 8.1: Research Activity Costs

Number	Type of Work	Unit	Quantity	Cost per Unit (€)	Total Cost (€)	Cost Reference
1	Preparation of the Project (Professors)	hr	40	26	1,040	(72)
2	Experimental Work (Researcher)	hr	216	20	4,320	(73)
3	Analysis of Results (Researcher)	hr	162	20	3,240	
4	Other Project Related Work (Researcher)	hr	162	20	3,240	
Total Cost (€)					11,840	

The cost of research activities was ELEVEN THOUSAND EIGHT HUNDRED AND FOURTY EUROS.

This estimate was made using the average salary paid to professor’s and researchers in Spain and is based upon the average hours worked per week on the project.

8.2 Equipment Costs

Cost of equipment and partial cost of their use are shown in Table 8.2.

Table 8.2: Equipment Costs

Number	Equipment	Unit	Quantity	Cost per Unit (€)	Partial Cost (€)	Cost Reference
1	Sterlitech Stirred Cell	Unit	1	2,831.34	2,831.34	(74)
2	Magnetic Stirrer*	Unit	1	978.67	22.02	(75)
3	Measuring Balance*	Unit	1	540	12.15	(76)
4	HPLC Equipment	Unit	1	N/A	N/A	-
5	Conductivity and pH Meter*	Unit	1	1877.87	9.39	(77)
Total Cost (€)					2,874.90	

The cost of equipment was TWO THOUSAND EIGHT HUNDRED AND SEVENTY FOUR EUROS AND NINETY CENTS.

The cost of HPLC equipment could not be found, as no commercial prices were available at the time of writing.

The partial cost of the equipment denoted with an '*' was calculated using Equation 8.1. The number of years taken for depreciation was estimated to be 10 years for all equipment.

$$Partial\ Cost = \frac{Months\ of\ Use}{12 * Years\ of\ Depreciation} * (Equipment\ cost) * \%\ Use \qquad \text{Equation 8.1}$$

8.3 Consumables Costs

The cost of chemicals and other consumables are shown in Table 8.3.

Table 8.3: Consumables Costs

Number	Consumable	Unit	Quantity	Cost per Unit (€)	Total Cost (€)	Cost Reference
1	BPA	250 g	0.074	173	0.05	(78)
2	NaCl	500 g	20	9.95	0.40	(79)
3	Glucose	kg	0.018 (g)	32.80	Negligible	(80)
4	MgSO4	kg	0.002	111	0.22	(81)
5	NaSO4	kg	0.015	39.50	0.59	(82)
6	NaOH	kg	0.044	35.24	1.55	(83)
7	Nitrogen	Vessel	79.3 (g)	863	0.07	(84)
8	NP030 Membrane	Membrane Sheet	2	23.71	47.42	(85)

9	NF270 Membrane	Membrane Sheet	1	26.69	26.69	(86)
10	Sample Bottles	Bottle	144	0.23	33.12	(87)
11	500 ml beaker	6 – Beaker pack	2 Beakers	10.37	3.46	(88)
12	250 ml beaker	12 – Beaker pack	2 Beakers	13.83	2.31	
13	100 ml beaker	12 – Beaker pack	2 Beakers	9.24	1.54	
14	50 ml beaker	12 – Beaker Pack	2 Beakers	8.68	1.45	
15	25 ml beaker	12 – Beaker Pack	2 Beakers	7.59	1.27	
16	Disposable Syringes	100 Syringes	25 Syringes	18.10	4.53	(89)
17	HPLC Sample Bottles	100 Bottles	180 Bottles	6.38	11.48	(90)
18	1 L volumetric flask	2 – Flask Pack	5 Flasks	23	57.50	(91)
19	500 ml volumetric flask	2 – Flasks Pack	4 Flasks	16	32	
20	200 ml graduated cylinder	Measuring Cylinder	1 Cylinder	11.06	11.06	(92)
21	100 ml graduated cylinder	Measuring Cylinder	1 Cylinder	6.71	6.71	
22	50 ml graduated cylinder	Measuring Cylinder	1 Cylinder	6.17	6.17	

23	25 ml graduated cylinder	Measuring Cylinder	1 Cylinder	5.95	5.95	
Total Cost (€)					255.54	

The cost of consumable materials was TWO HUNDRED AND FIFTY FIVE EUROS AND FIFTY FOUR CENTS.

8.4 Budget Summary

The direct costs from the study are shown in Table 8.4.

Table 8.4: Direct Costs for Project

Type of Costs	Cost
Research Activity Cost (€)	11,840
Equipment (€)	2,874.90
Consumables (€)	255.54
Total Direct Cost (€)	14,970.44

Indirect costs were taken as an estimate of 25% of the total estimated cost (93), to cover utilities such as electricity, software usage etc. VAT was assumed to be at a rate of 20%. The final cost for the project is shown in Table 8.5.

Table 8.5: Total Costs for Project

Type of Costs	Cost
Direct Costs (€)	14,970.44
Indirect Costs (€)	3742.61
VAT (20% of Direct and Indirect Costs) (€)	3742.61
Final Project Cost (€)	22,455.66

The final cost of the entire project was TWETNY TWO THOUSAND FOUR HUNDRED AND FIFTY FIVE EUROS AND SIXTY SIX CENTS.

8.5 Analysis of Economic Viability of the Project

The project itself was economical viable, with its costs justified by the need to investigate this area of microplastic removal and the importance of this work to the environment. The cost if this research were continued or another screening study carried out could vary; it would depend on how many experiments were performed, and if any were repeated. Similarly, the work required to prepare and research the subject of BPA nanofiltration could be reduced, as this report provides a suitable background knowledge for any researchers new to the field.

The main equipment, the Sterlitech stirred cell, and auxiliary items such as beakers and flasks have already been purchased by the research group, so this would help reduce costs in the future for similar studies.

As the future research proposed is optimisation of BPA removal via nanofiltration, the screening conducted in this study is likely to be less costly than the full optimisation study. This is due to the fact the optimisation study would require many more targeted experiments than were carried out in this study.

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89. Disposable syringe, with Luer fitting, 10 ml | Disposable syringes | Syringes and accessories | Liquid Handling | Labware | Carl Roth - International [Internet]. [cited 2022 May 1]. Available from: https://www.carlroth.com/com/en/disposable-syringes/disposable-syringe-with-luer-fitting/p/0058.1

90. Short Thread 9mm Amber Glass 1.5mL HPLC Autosampler Vials w/ Writing Patch - Economy 100/pk, CV1831 [Internet]. [cited 2022 May 1]. Available from: https://scientificfilters.com/chromatography-vials-caps-septa/screw-neck-vials-cv1831

91. Volumetric flask class A with plastic stopper, LBG [Internet]. Labbox Export. [cited 2022 May 1]. Available from: https://ien.labbox.com/product/volumetric-flask-class-a-with-plastic-stopper-lbg/

92. Measuring cylinder hexagonal base, class A, GLASSCO [Internet]. Labbox Export. [cited 2022 May 1]. Available from: https://ien.labbox.com/product/measuring-cylinder-hexagonal-base-class-a-glassco/

93. Indirect costs in Horizon 2020 | FFG [Internet]. [cited 2022 May 2]. Available from: https://www.ffg.at/en/europe/legalandfinancialmatters/h2020_indirect-costs

Appendices

Appendix 4.1 – Sterlitech Cell Diagram

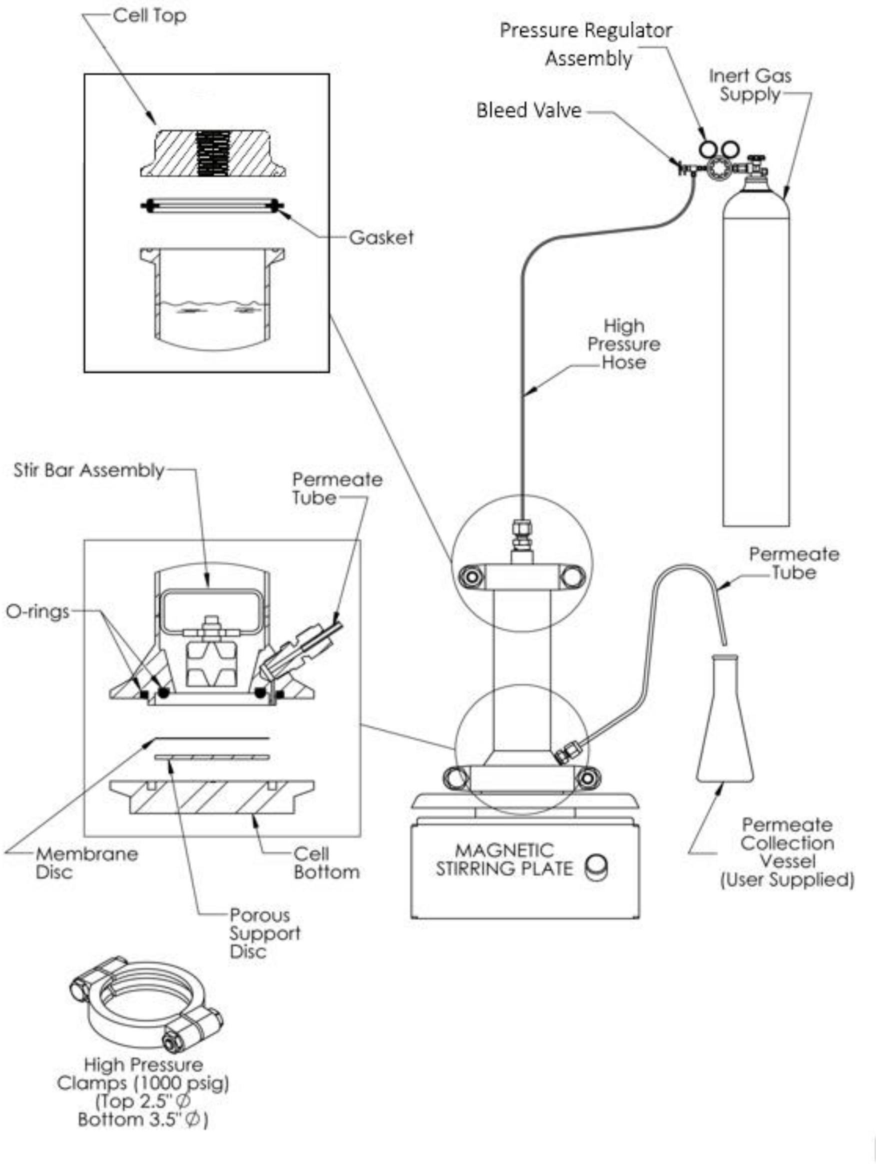


Figure 9.1: Sterlitech Cell Setup (71)

Appendix 4.2 – Assembly and Operation of Sterlitech Stirred Cell Guide

Before the stirred cell can be used, it must be assembled. This procedure is described below. Figures 9.2 – 9.12 show the visualisation of this process.

Assembly

1. The pieces of the cell should be laid out as shown, to ensure nothing is missing.

Figure 9.2: Cell Pieces

2. The two O-rings should be wetted with water or the solution that is going to be filtered. They are then fitted onto the bottom of the main cell body, with the smaller O-ring fitting on the inner grove, and the large O-ring on the outer groove.

Figure 9.3: O-ring Insertion

3. The piece of membrane that has been cut to size is then placed over the opening at centre of the cell, where the O-rings have just been placed. The active side of the membrane should be facing into the cell, so that it will contact the solution.

Figure 9.4: Membrane Insertion

4. The membrane support disk is then placed over the membrane to hold it in place.

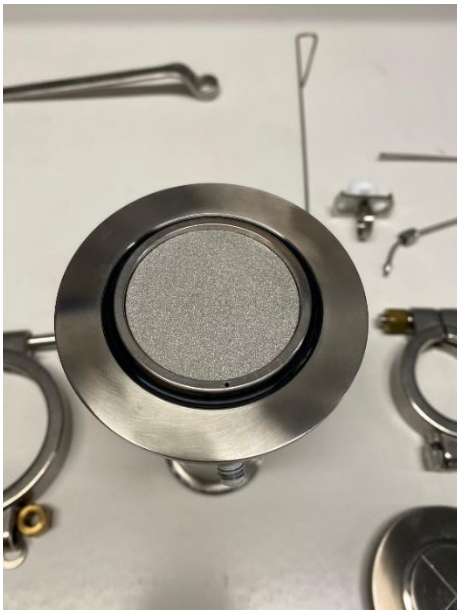


Figure 9.5: Membrane Support Disk Insertion

5. The bottom of the cell can now be aligned with the cell body and pressed together.


Figure 9.6: Bottom of Cell Body

6. The larger of the clamps is then attached to the bottom of the cell to hold the two pieces together. On the holes for the bolts, there is a raised edge on the side to indicate this is where the bolt's head should lie. The nuts on the bolts should be tightened securely, using a wrench if required. However, care should be taken not to over tighten them, as this may cause damage to the equipment, in particular the nuts.


Figure 9.7: Tightening of Bottom of Cell Body

7. The permeate tube can then be attached to the port on the side of the cell body. If required a wrench can be used to tighten it.

Figure 9.8: Attachment of Permeate Tube

8. The magnetic stirrer is then lowered into the cell body using the hook provided. It should sit as shown in the figure. The solution to be filtered should be poured into the cell at this stage.

Figure 9.9: Lowering of Magnetic Stirrer

Figure 9.10: Magnetic Stirrer in Place

9. The black gasket should then be fitted to the top of the cell. The top section can then be aligned and placed onto the cell body.

Figure 9.11: Alignment of Cell's Top Section

10. The smaller clamp can then be used to clamp the top of the cell together. Again, the nuts on the bolts should be tightened securely, using a wrench if required, with care taken not to overtighten.

Figure 9.12: Tightening of Top Cell Section

Operation of the Stirred Cell

The following instructions detail how to prepare the stirred cell for operation. Safety goggles should be worn at all times of operation for protection in case of hose breaking free. Figure 9.13 –9.21 show the visualisation of this process.

1. The hose from the nitrogen tank should be wound around the metal bar on the worktop and be held in place by a clamp. If possible, it should be tied to the metal bar.

Figure 9.13: Connecting Cell to Pressurised Nitrogen

2. The hose should then be connected to the cell. A wrench can be used to tighten it.

Figure 9.14: Hose Connection

3. The cell should then be placed on a magnetic stirrer (which is turned off). Meanwhile, a permeate collection beaker should be placed on a balance, and underneath the permeate tube to collect the permeate.

Figure 9.15: Cell and Magnetic Stirrer Placement

4. A laptop (or computer) should be connected to the balance, so that the mass of permeate collected can be recorded and monitored. This is important, as if the liquid within the cell drops below a certain level, then the equipment may be damaged due to the pressurised nitrogen.

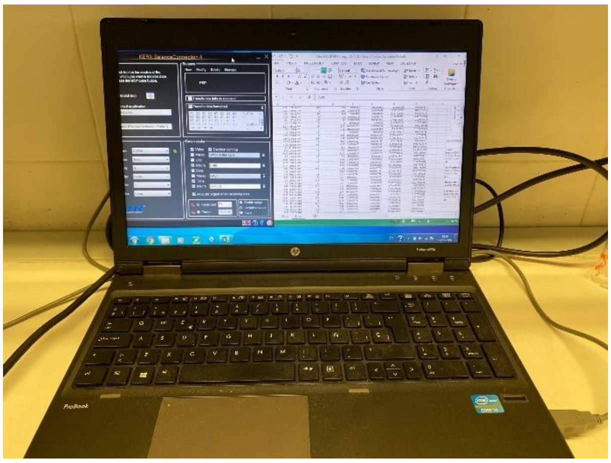


Figure 9.16: Connection of Electronic Balance to Laptop

5. The magnetic stirrer can now be turned on.

Figure 9.17: Magentic Stirring Initiated

6. The purge valve should be turned to the closed position.

Figure 9.18: Closing of Purge Valve

7. The valve on the pressurised nitrogen tank can then be turned to the open position, this is done by turning it anti-clockwise.

Figure 9.19: Opening of Nitrogen Tank

8. The gauge shown can then be used to set the pressure of the system to the required pressure, by turning the valve. Once at the required pressure, the circled valve can be opened to pressurise the cell, and the filtration will begin.

Figure 9.20: Pressuring the System

9. Once the filtration process is complete, it is necessary to depressurise the cell. This should be done by first closing off the valve to the stirred cell. The pressure gauge should then be set to 0, and the nitrogen tank valve, see step 7, should be turned off. The relief valve, shown in step 6, can then be used to purge the nitrogen from the system. It will then be safe to disassemble the stirred cell. The cell should not be disassembled, or the clamps removed while it is still pressurised.

Figure 9.21: Depressurised System

Appendix 4.3 – HPLC Operation Guide

This is a written procedure for use of the HPLC equipment, for analysis of BPA samples collected during experimental runs.

Note – before every use, the water that is used in the mobile phase (phase A) should be filtered using a vacuum filter. The filter can be used 2-3 times before being replaced.

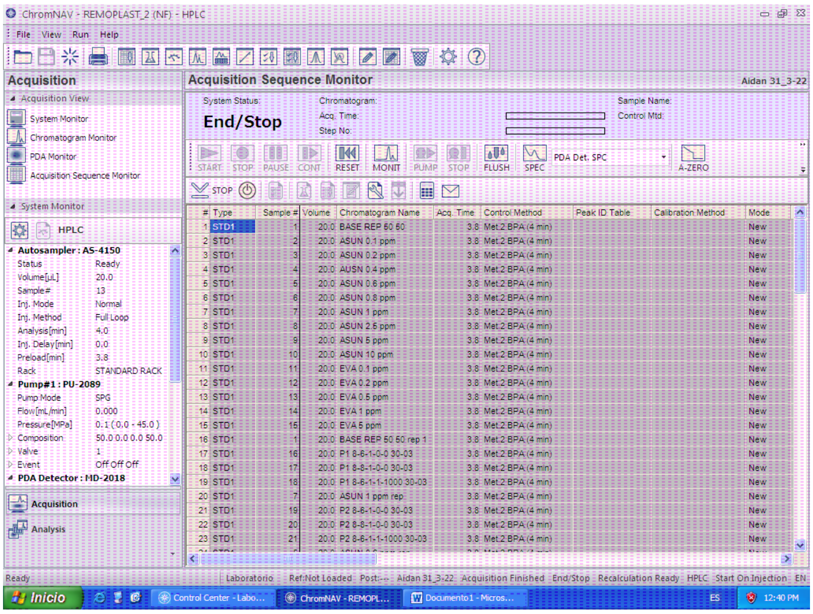
Process for Turning on System and Creating Calibration Line

1. The following equipment should all be turned on: the mobile phase pump, the chromatographic column, the PDA detector, the autosampler and the computer.
2. Open the software ChromNAV.
3. Select the mode of operation – "HPLC".
4. The folder called "REMOPLASTS_2(NF)" must then be selected, as this contains the method to measure BPA concentrations. This gives the functions to measure and analyse the results.
5. The pump should be turned on, and the valve to the mobile phase opened. Set the flowrate to 3 ml/min, set to phase A, and allow the water to flow for 2 to 3 minutes into a beaker. This is to purge the stream. After this is completed, change the phase to D to carry out a purge of acetonitrile in the same fashion.
6. Once the purge is complete, dispose of the liquid in the beaker into the waste bottle.
7. To start the calibration of the equipment, click the "Run" button then select "Monitor baseline". Choose the option "BPA Met.2" and input a time of 60 minutes. The HPLC will then begin to calibrate and create a calibration line. Take note of the time the run is started at, and during the run the pressure should be monitored. This is to ensure there is no blockage in the pre-column filter which may cause damage. The pressure should be around 16-20 MPa.
8. The calibration line can be seen by clicking "Chromatogram Monitor" on the left side of the screen.
9. After 60 minutes, the baseline is complete, and samples can then be tested.

Analysing samples

1. Once the equipment is operational and a calibration line has been created, samples can be tested.
2. Ensure the mobile phases are set at 50% water and 50% acetonitrile, and that the wavelength of detection is set to 214 nm.
3. BPA is found to have a retention time of 2.5 minutes, so the area under the peak at this point on the graph is related to the concentration of BPA in the sample. Thus, the concentration can be measure by using the area under the graph.
4. Samples should be prepared using small HPLC vials. If measuring real wastewater samples, the feed and retentate solutions should be measured out after being filtered using 0.2 µm RephiQuik syringe filters. This is to prevent fouling within the HPLC equipment.
5. Before testing the samples, information regarding each one should be input into the software. To do this select the "Edit acquisition sequence" button.
6. Then input the following data for each one
   Type – STD1.

Sample – The numbered position that the sample is sitting in within the tray.
Volume – 20 µl.
Chromatogram name – The name given to the sample to identify it.
Acquisition time – 3.8 minutes.
Control method – Met.2 BPA (4 min).
Mode – New.
Then save the sequence under an appropriate name.
An example sequence is shown in Figure 9.22.



System Status: End/Stop
Chromatogram:
Acq. Time:
Step No:
Sample Name:
Control Mtd:

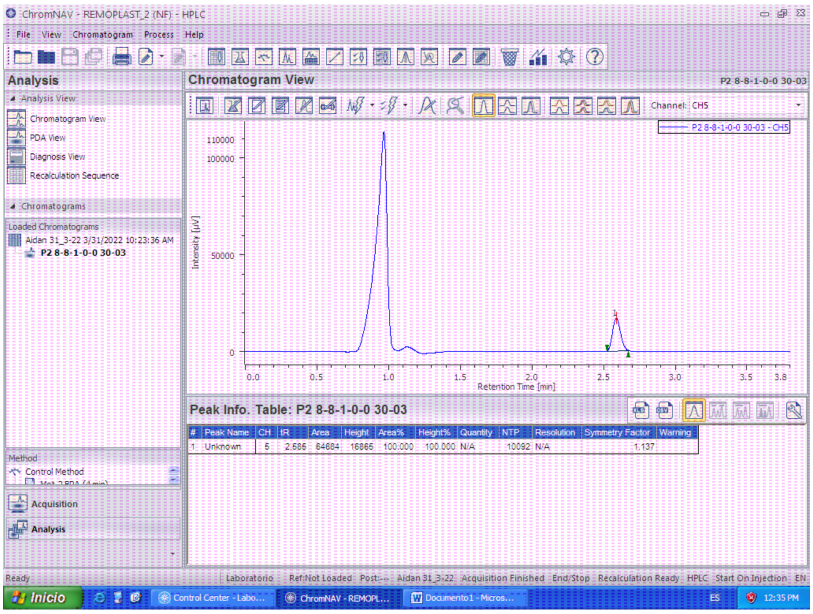
Autosampler : AS-4150
Status Ready
Volume[µL] 20.0
Sample# 13
Inj. Mode Normal
Inj. Method Full Loop
Analysis[min] 4.0
Inj. Delay[min] 0.0
Preload[min] 3.8
Rack STANDARD RACK
Pump#1 : PU-2089
Pump Mode SPG
Flow[mL/min] 0.000
Pressure[MPa] 0.1 (0.0 - 45.0)
Composition 50.0 0.0 0.0 50.0
Valve 1
Event Off Off Off
PDA Detector : MD-2018

#	Type	Sample #	Volume	Chromatogram Name	Acq. Time	Control Method	Peak ID Table	Calibration Method	Mode
1	STD1	1	20.0	BASE REP 50 50	3.8	Met.2 BPA (4 min)			New
2	STD1	2	20.0	ASUN 0.1 ppm	3.8	Met.2 BPA (4 min)			New
3	STD1	3	20.0	ASUN 0.2 ppm	3.8	Met.2 BPA (4 min)			New
4	STD1	4	20.0	AUSN 0.4 ppm	3.8	Met.2 BPA (4 min)			New
5	STD1	5	20.0	ASUN 0.6 ppm	3.8	Met.2 BPA (4 min)			New
6	STD1	6	20.0	ASUN 0.8 ppm	3.8	Met.2 BPA (4 min)			New
7	STD1	7	20.0	ASUN 1 ppm	3.8	Met.2 BPA (4 min)			New
8	STD1	8	20.0	ASUN 2.5 ppm	3.8	Met.2 BPA (4 min)			New
9	STD1	9	20.0	ASUN 5 ppm	3.8	Met.2 BPA (4 min)			New
10	STD1	10	20.0	ASUN 10 ppm	3.8	Met.2 BPA (4 min)			New
11	STD1	11	20.0	EVA 0.1 ppm	3.8	Met.2 BPA (4 min)			New
12	STD1	12	20.0	EVA 0.2 ppm	3.8	Met.2 BPA (4 min)			New
13	STD1	13	20.0	EVA 0.5 ppm	3.8	Met.2 BPA (4 min)			New
14	STD1	14	20.0	EVA 1 ppm	3.8	Met.2 BPA (4 min)			New
15	STD1	15	20.0	EVA 5 ppm	3.8	Met.2 BPA (4 min)			New
16	STD1	1	20.0	BASE REP 50 50 rep 1	3.8	Met.2 BPA (4 min)			New
17	STD1	16	20.0	P1 8-6-1-0-0 30-03	3.8	Met.2 BPA (4 min)			New
18	STD1	17	20.0	P1 8-8-1-0-0 30-03	3.8	Met.2 BPA (4 min)			New
19	STD1	18	20.0	P1 8-6-1-1-1000 30-03	3.8	Met.2 BPA (4 min)			New
20	STD1	7	20.0	ASUN 1 ppm rep	3.8	Met.2 BPA (4 min)			New
21	STD1	19	20.0	P2 8-6-1-0-0 30-03	3.8	Met.2 BPA (4 min)			New
22	STD1	20	20.0	P2 8-8-1-0-0 30-03	3.8	Met.2 BPA (4 min)			New
23	STD1	21	20.0	P2 8-6-1-1-1000 30-03	3.8	Met.2 BPA (4 min)			New

Ready
Laboratorio Ref:Not Loaded Post:--- Aidan 31_3-22 Acquisition Finished End/Stop Recalculation Ready HPLC Start On Injection EN

Figure 9.22: Acquisition Sequence Example

7. Then click “Load acquisition sequence” and start the run.
8. Once completed, the chromatograms can be opened in the “Analysis” mode and selecting “Open chromatogram”. An example chromatogram is shown in Figure 9.23

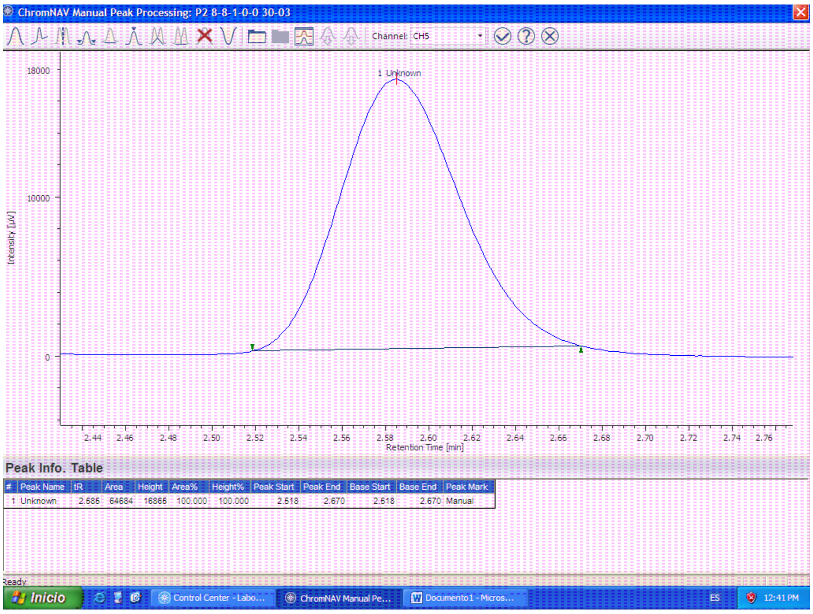


Peak Info. Table: P2 8-8-1-0-0 30-03

#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	2.585	64684	16865	100.000	100.000	N/A	10092	N/A	1.137	

Figure 9.23: Chromatogram Example

9. When the chosen chromatogram is selected, the "Manual peak processing option" should be selected.
10. From here, select "Add peak" and this allows the peak at approximately 2.5 minutes to be analysed, to allow the exact retention time and area under the curve to be calculated. This can be repeated for all chromatograms required. An example of this is shown in Figure 9.24.



Peak Info. Table

#	Peak Name	tR	Area	Height	Area%	Height%	Peak Start	Peak End	Base Start	Base End	Peak Mark
1	Unknown	2.585	64684	16865	100.000	100.000	2.518	2.670	2.518	2.670	Manual

Figure 9.24: Manual Peak Processing Example

Appendix 4.4 – MatLab Code for NF270 DSPM

```
clc, clear, close all
%% Hindrance factor as a function of lambda
lambdas = 0:0.01:1;
void = zeros(size(lambdas)); Kd = void; Kc = void; phi = void;
for i = 1:length(lambdas)
    [Kd(i),Kc(i),G0,phi(i)] = hindrance_factors(lambdas(i));
end
figure, hold on
plot(lambdas,Kd)
plot(lambdas,Kc)
plot(lambdas,phi)
ylim([0 Inf])
xlabel('\lambda')
legend({'K_d','K_c','\phi'},'Location','Best')


%% MEMBRANE DATA
% Membrane water permeability
Lp = 2.223E-11; %m3/(m2*s*Pa)
% DSPM parameteres
rp_min = 0.47e-9;    %m, Maximum pore radius
rp_max = 0.99e-9;    %m, Minimum pore radius
rp_mean = 0.71e-9;   %m, Mean pore radius
rp_std = 0.14e-9;    %m,  Standard deviation

rp_LB = rp_mean-rp_std;    %m, Pore radius
rp_UB = rp_mean+rp_std;    %m, Pore radius

rp_LB = rp_mean*sqrt(1.15);    %m, Pore radius
rp_UB = rp_mean*sqrt(0.85);    %m, Pore radius


dx_Ak = 1.1e-6; %m, Ratio of the thickness layer to pore fractional area

%% COMPONENT DATA
% Name of compounds
comps{1} = 'BPA (0 ppm NaCl)';
comps{2} = 'BPA (1000 ppm NaCl)';
% comps{3} = 'glucose';

% Stokes radius (Fig 4 Transportation characteristics of BPA.pdf=
rS_BPA_0000NaCl = 0.47E-9;  %m, BPA at NaCl=0 ppm
rS_BPA_1000NaCl = 0.33E-9;  %m, BPA at NaCl=1000 ppm
rS_BPA_2000NaCl = 0.36E-9;  %m, BPa at NaCl=2000 ppm (see foot note)
%Table (2 (Stokes radius glucose.pdf in literature gives rS = 0.36 nm


%% CONDITIONS

T = 298.15; %K

%% THEORETICAL CURVES
Jv = (0:0.05:20)'*1e-6; %m3/(m2*s*Pa) % ADJUST RANGE
R_BPA_model = zeros(length(Jv),1);
R_BPA_0000NaCl_model_max = R_BPA_model;
R_BPA_0000NaCl_model_mean = R_BPA_model;
```

```
R_BPA_0000NaCl_model_min = R_BPA_model;

R_BPA_1000NaCl_model_max = R_BPA_model;
R_BPA_1000NaCl_model_mean = R_BPA_model;
R_BPA_1000NaCl_model_min = R_BPA_model;

R_BPA_2000NaCl_model_max = R_BPA_model;
R_BPA_2000NaCl_model_mean = R_BPA_model;
R_BPA_2000NaCl_model_min = R_BPA_model;


for i = 1:length(Jv)
   % BPA at NaCl 0 ppm
     %Maximum retention for minimum Stokes radius
     R_BPA_0000NaCl_model_max(i) = R_DSPM_uc(Jv(i),T,Lp,rp_LB,rS_BPA_0000NaCl);

     %Retention for mean Stokes radius
     R_BPA_0000NaCl_model_mean(i) = R_DSPM_uc(Jv(i),T,Lp,rp_mean,rS_BPA_0000NaCl);
     %Maximum retention for maximum Stokes radius
     R_BPA_0000NaCl_model_min(i) = R_DSPM_uc(Jv(i),T,Lp,rp_UB,rS_BPA_0000NaCl);

   % BPA at NaCl 1000 ppm
     %Maximum retention for minimum Stokes radius
     R_BPA_1000NaCl_model_max(i) = R_DSPM_uc(Jv(i),T,Lp,rp_LB,rS_BPA_1000NaCl);
     %Retention for mean Stokes radius
     R_BPA_1000NaCl_model_mean(i) = R_DSPM_uc(Jv(i),T,Lp,rp_mean,rS_BPA_1000NaCl);
     %Maximum retention for maximum Stokes radius
     R_BPA_1000NaCl_model_min(i) = R_DSPM_uc(Jv(i),T,Lp,rp_UB,rS_BPA_1000NaCl);

   % BPA at NaCl 2000 ppm
     %Maximum retention for minimum Stokes radius
     R_BPA_2000NaCl_model_max(i) = R_DSPM_uc(Jv(i),T,Lp,rp_LB,rS_BPA_2000NaCl);
     %Retention for mean Stokes radius
     R_BPA_2000NaCl_model_mean(i) = R_DSPM_uc(Jv(i),T,Lp,rp_mean,rS_BPA_2000NaCl);
     %Maximum retention for maximum Stokes radius
     R_BPA_2000NaCl_model_min(i) = R_DSPM_uc(Jv(i),T,Lp,rp_UB,rS_BPA_2000NaCl);

end

%% EXPERIMENTAL DATA
factor = 2.778e-7; %kg/(m2·h) --> m3/(m2*s)
D = [
    33.1561649 0.7227      0.8901
    68.52054795     0.4677 0.6479
    32.72876712     0.6982 0.8169
    64.49315068     0.9137 0.8320
    24.9260274      0.6461 0.6397
    61.10136986     0.6414 0.3835
    24.30684932     0.6028 0.4637
    49.79726027     0.7153 0.5011
    34.98630137     0.7630 0.8810
    65.01917808     0.7257 0.8667
    34.21369863     0.5276 0.8755
    65.22739726     0.6416 0.8513
    28.3890411      0.5804 0.6360
    58.2739726      0.6416 0.6510
    24.63561644     0.7288 0.5452
    51.66575342     0.7154 0.5569];
```

```
% conditions 1: pH = 6; C_NaCl = 0 mg/L; glucose = 0 mg/L
r = 1:2;
Jv_0NaCl_pH6 = D(r,1)*factor;
R_BPA_0NaCl_pH6  = D(r,2);
R_NaCl_0NaCl_pH6  = D(r,3);

% conditions 2: pH = 6; C_NaCl = 0 mg/L; glucose = 1 mg/L
r = 3:4;
Jv_0NaCl_1Gluc_pH6 = D(r,1)*factor;
R_BPA_0NaCl_1Gluc_pH6  = D(r,2);
R_NaCl_0NaCl_1Gluc_pH6  = D(r,3);


% conditions 3: pH = 6; C_NaCl = 1000 mg/L
r = 5:6;
Jv_1000NaCl_pH6 = D(r,1)*factor;
R_BPA_1000NaCl_pH6  = D(r,2);
R_NaCl_1000NaCl_pH6  = D(r,3);

% conditions 4: pH = 6; C_NaCl = 2000 mg/L
r = 7:8;
Jv_2000NaCl_pH6 = D(r,1)*factor;
R_BPA_2000NaCl_pH6  = D(r,2);
R_NaCl_2000NaCl_pH6  = D(r,3);

% conditions 5: pH = 8; C_NaCl = 0 mg/L; glucose = 0 mg/L
r = 9:10;
Jv_0NaCl_pH8 = D(r,1)*factor;
R_BPA_0NaCl_pH8  = D(r,2);
R_NaCl_0NaCl_pH8  = D(r,3);

% conditions 6: pH = 8; C_NaCl = 0 mg/L; glucose = 1 mg/L
r = 11:12;
Jv_0NaCl_1Gluc_pH8 = D(r,1)*factor;
R_BPA_0NaCl_1Gluc_pH8  = D(r,2);
R_NaCl_0NaCl_1Gluc_pH8  = D(r,3);

% conditions 7: pH = 8; C_NaCl = 1000 mg/L
r = 13:14;
Jv_1000NaCl_pH8 = D(r,1)*factor;
R_BPA_1000NaCl_pH8  = D(r,2);
R_NaCl_1000NaCl_pH8  = D(r,3);

% conditions 8: pH = 8; C_NaCl = 2000 mg/L
r = 15:16;
Jv_2000NaCl_pH8 = D(r,1)*factor;
R_BPA_2000NaCl_pH8  = D(r,2);
R_NaCl_2000NaCl_pH8  = D(r,3);



%% REPRESENTATION

label_x = 'Flux (m^3·m^{-2}·s^{-1})';
label_y = 'Retention (%)';
```

```
figure

subplot(1,3,1), hold on
    title('BPA = 1 mg/L, NaCl = 0 mg/L')

    plot(Jv,R_BPA_0000NaCl_model_mean*100,'k-','LineWidth',1)
    plot(Jv_0NaCl_pH6,R_BPA_0NaCl_pH6*100,'bo','Markersize',6)
    plot(Jv_0NaCl_1Gluc_pH6,R_BPA_0NaCl_1Gluc_pH6*100,'d','Markersize',6)
    plot(Jv_0NaCl_pH8,R_BPA_0NaCl_pH8*100,'rv','Markersize',6)
    plot(Jv_0NaCl_1Gluc_pH8,R_BPA_0NaCl_1Gluc_pH8*100,'+','Markersize',6)

    plot(Jv,R_BPA_0000NaCl_model_max*100,'k--','LineWidth',0.25)
    plot(Jv,R_BPA_0000NaCl_model_min*100,'k--','LineWidth',0.25)

    xlabel(label_x), ylabel(label_y)

    ylim([0 100])

    legend({'BPA model',...
            'BPA exp. pH=6 (0 mg/L Glucose)',...
            'BPA exp. pH=6 (1 mg/L Glucose)',...
            'BPA exp. pH=8 (0 mg/L Glucose)',...
            'BPA exp. pH=8 (1 mg/L Glucose)'},'Location','southoutside')

subplot(1,3,2), hold on
    title('BPA = 1 mg/L, NaCl = 1,000 mg/L')

    plot(Jv,R_BPA_1000NaCl_model_mean*100,'k-','LineWidth',1)
    plot(Jv_1000NaCl_pH6,R_BPA_1000NaCl_pH6*100,'bo','Markersize',6)
    plot(Jv_1000NaCl_pH8,R_BPA_1000NaCl_pH8*100,'rv','Markersize',6)

    plot(Jv,R_BPA_1000NaCl_model_max*100,'k--','LineWidth',0.25)
    plot(Jv,R_BPA_1000NaCl_model_min*100,'k--','LineWidth',0.25)

    xlabel(label_x), ylabel(label_y)

    legend({'BPA model',...
            'BPA exp. pH=6 ',...
            'BPA exp. pH=8 '},'Location','southoutside')

    ylim([0 100])


subplot(1,3,3), hold on
    title('BPA = 1 mg/L, NaCl = 2,000 mg/L')

    plot(Jv,R_BPA_2000NaCl_model_mean*100,'k-','LineWidth',1)
    plot(Jv_2000NaCl_pH6,R_BPA_2000NaCl_pH6*100,'bo','Markersize',6)
    plot(Jv_2000NaCl_pH8,R_BPA_2000NaCl_pH8*100,'rv','Markersize',6)

    plot(Jv,R_BPA_2000NaCl_model_max*100,'k--','LineWidth',0.25)
    plot(Jv,R_BPA_2000NaCl_model_min*100,'k--','LineWidth',0.25)

    xlabel(label_x), ylabel(label_y)

    ylim([0 100])
```

```
    legend({'BPA model',...
            'BPA exp. pH=6 ',...
            'BPA exp. pH=8 '},'Location','southoutside')




%% **********************************************************************
function visco = visco_water(T)
    visco = 0.89E-3*T^0; %Pa·s  % LOOK FOR MORE ACCURATE EXPRESSION
end

%% **********************************************************************

function D = diffusivity(T,rS)
    kB = 1.3806505E-23; %J/K, Boltzmann constant
    D = (kB*T)./((6*pi*visco_water(T)).*rS);
end

%% **********************************************************************

function R = R_DSPM_uc(Jv,T,Lp,rp,rS)
    % Rejection estimated by DSPM model for uncharged components
    lambda = rS/rp;
    [Kd,Kc,~,phi] = hindrance_factors(lambda);
    Kcphi = Kc*phi;
    D = diffusivity(T,rS);
    Pe = Kc^2*rp^2/(8*Lp*Kd*D*visco_water(T))*Jv;
    R = 1-Kcphi/(1-(1-Kcphi)*exp(-Pe));
end


%% **********************************************************************
function [Kd,Kc,G0,phi_esf] = hindrance_factors(lambda)

lambda2 = lambda*lambda;
lambda3 = lambda2*lambda;

if  lambda <0.8
    Kd = 1.0 - 2.3*lambda + 1.154*lambda2 + 0.224*lambda3;
    G0 = 1.0 + 0.054*lambda - 0.988*lambda2 + 0.441*lambda3;
else
    Kd = -0.105 + 0.318*lambda - 0.213*lambda2;
    G0 = -6.830 + 19.348*lambda - 12.518*lambda2;
end

if lambda<1.0
    phi_esf = (1.0 - lambda)^2;
else
    phi_esf = 0.0;
end

% Corrección del arrastre convectivo
Kc = (2.0 - phi_esf)*G0;

end
```

```
%% *********************************************************************
```

Appendix 5.1 – Raw Data for BPA Retention Calculations

Table 9.1: Raw Data from NP030 Experiments

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	Volumetric Flux (m^3/m^2s)	Feed BPA Conc. (mg/L)	1st Permeate BPA Conc. (mg/L)	2nd Permeate BPA Conc. (mg/L)	Retentate BPA Conc. (mg/L)
4	6	1	0	0	4.573E-06	0.578	0.289	0.303	0.345
8	6	1	0	0	7.448E-06	0.578	0.431	0.495	0.475
4	6	1	1	0	3.916E-06	0.346	0.324	0.236	0.346
8	6	1	1	0	6.431E-06	0.484	0.520	0.518	0.639
4	6	1	1	1000	4.164E-06	0.203	0.348	0.201	0.260
8	6	1	1	1000	6.371E-06	0.203	0.372	0.291	0.323
4	6	1	1	2000	4.158E-06	0.513	0.496	0.397	0.420
8	6	1	1	2000	6.780E-06	0.513	0.363	0.423	0.453
4	8	1	0	0	3.496E-06	0.427	0.387	0.386	0.350
8	8	1	0	0	6.319E-06	0.427	0.409	0.327	0.425
4	8	1	1	0	3.392E-06	0.405	0.021	0.176	0.228
8	8	1	1	0	6.073E-06	0.405	0.302	0.270	0.267
4	8	1	1	1000	3.424E-06	0.366	0.319	0.216	0.367
8	8	1	1	1000	6.086E-06	0.366	0.402	0.514	0.616
4	8	1	1	2000	3.241E-06	0.172	0.329	0.169	0.117
8	8	1	1	2000	5.785E-06	0.172	0.280	0.231	0.253

Table 9.2: Raw Data from NF270 Experiments

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	Volumetric Flux (m^3/m^2s)	Feed BPA Conc. (mg/L)	1st Permeate BPA Conc. (mg/L)	2nd Permeate BPA Conc. (mg/L)	Retentate BPA Conc. (mg/L)
4	6	1	0	0	9.262E-06	0.396	0.190	0.108	0.401
8	6	1	0	0	1.914E-05	0.396	0.205	0.303	0.604
4	6	1	1	0	9.144E-06	0.433	0.199	0.120	0.409
8	6	1	1	0	1.802E-05	0.433	0.169	0.049	0.640
4	6	1	1	1000	6.969E-06	0.516	0.195	0.177	0.567
8	6	1	1	1000	1.708E-05	0.516	0.247	0.251	0.809
4	6	1	1	2000	6.774E-06	0.437	0.218	0.205	0.524
8	6	1	1	2000	1.346E-05	0.437	0.077	0.178	0.657
4	8	1	0	0	9.781E-06	0.305	0.152	0.101	0.440
8	8	1	0	0	1.818E-05	0.305	0.170	0.131	0.522
4	8	1	1	0	9.550E-06	0.519	0.281	0.285	0.616
8	8	1	1	0	1.821E-05	0.519	0.233	0.288	0.867
4	8	1	1	1000	7.920E-06	0.445	0.185	0.132	0.321
8	8	1	1	1000	1.626E-05	0.445	0.175	0.130	0.406
4	8	1	1	2000	6.866E-06	0.528	0.285	0.156	0.587
8	8	1	1	2000	1.440E-05	0.528	0.266	0.197	0.730

Table 9.3: Raw Data from Discarded NP030 Experiments

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	Volumetric Flux (m^3/m^2s)	Feed BPA Conc. (mg/L)	1st Permeate BPA Conc. (mg/L)	2nd Permeate BPA Conc. (mg/L)	Retentate BPA Conc. (mg/L)
4	6	1	0	0	4.607E-06	0.287	0.266	0.204	0.209
8	6	1	0	0	6.773E-06	0.287	0.344	0.308	0.264
4	6	1	1	0	3.999E-06	0.484	0.257	0.180	0.216
4	6	1	1	2000	4.062E-06	1.264	0.423	0.402	0.356
8	6	1	1	2000	5.680E-06	1.264	0.298	0.271	0.158
8	6	1	1	0	6.614E-06	0.346	0.370	0.372	0.393

Table 9.4: Raw Data from Discarded NF270 Experiments

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	Volumetric Flux (m^3/m^2s)	Feed BPA Conc. (mg/L)	1st Permeate BPA Conc. (mg/L)	2nd Permeate BPA Conc. (mg/L)	Retentate BPA Conc. (mg/L)
8	6	1	0	0	1.956E-05	0.877	0.320	0.376	1.237
8	8	1	0	0	1.880E-05	0.877	0.443	0.481	1.458
8	6	1	1	1000	1.620E-05	0.241	0.152	0.208	0.471

Appendix 5.2 – Example Calculations of BPA and Salt Retention

The calculation for the retention of BPA in the first experiment for the NF270 membrane is shown below. The relevant data required is shown in Table 9.5.

Table 9.5: Data for Sample BPA Retention Calculations

Feed BPA Conc. (mg/L)	1st Permeate BPA Conc. (mg/L)	2nd Permeate BPA Conc. (mg/L)	Retentate BPA Conc. (mg/L)	Initial Feed Volume (ml)	First Permeate Volume (ml)	Second Permeate Volume (ml)
0.396	0.190	0.108	0.401	200	49	12

The recovery for the first permeate, Y_1, was calculated.

$$Y_1 = \frac{V_{p1}}{V_{f0}} = \frac{49}{200} = 0.245$$

The retention of BPA for the first permeate, R_1, was then calculated.

$$R_1 = \frac{-\ln\left(\frac{1-\frac{C_{p1}}{C_{f0}}Y_1}{1-Y_1}\right)}{\ln(1-Y_1)} = \frac{-\ln\left(\frac{1-\frac{0.190}{0.396}*0.245}{1-0.245}\right)}{\ln(1-0.245)} = 0.555$$

$$R_1 = 0.555 * 100\% = 55.5\%$$

The volume of feed left after collection of the first permeate is then calculated.

$$V_{f1} = V_{f0} - V_{p1} = 200 - 49 = 151ml$$

The recovery for the second permeate, Y_2, was then calculated.

$$Y_2 = \frac{V_{p2}}{V_{f1}} = \frac{12}{151} = 0.0795$$

The retention of the second permeate, R_2, was then calculated.

$$R_2 = \frac{\ln\left(1-Y_2\left(1-\frac{C_{p2}}{C_{f2}}\right)\right)}{\ln(1-Y_2)} = \frac{\ln\left(1-0.0795\left(1-\frac{0.108}{0.401}\right)\right)}{\ln(1-0.0795)} = 0.722$$

$$R_2 = 0.722 * 100\% = 72.2\%$$

The data required for calculation of salt retentions for the same experiment is seen in Table 9.6.

Table 9.6: Data for Sample Salt Retention Calculations

Feed Conductivity (µS/cm)	1st Permeate Conductivity (µS/cm)	2nd Permeate Conductivity (µS/cm)	Retentate Conductivity (µS/cm)
8.42	7.12	6.34	59.83

The recoveries calculated for the BPA retentions are used again here. The first permeate salt retention was calculated.

$$R_{S,1} = \frac{-\ln\left(\dfrac{1-\dfrac{\Lambda_{p1}}{\Lambda_{f0}} * Y_1}{1-Y_1}\right)}{\ln(1-Y_1)} = \frac{-\ln\left(\dfrac{1-\dfrac{7.12}{8.42} * 0.245}{1-0.245}\right)}{\ln(1-0.245)} = 0.174$$

$$R_{S,1} = 0.174 * 100\% = 17.4\%$$

The second permeate retention was then calculated.

$$R_{S,2} = \frac{\ln\left(1-Y_2\left(1-\dfrac{\Lambda_{p2}}{\Lambda_{f2}}\right)\right)}{\ln(1-Y_2)} = \frac{\ln\left(1-0.0795\left(1-\dfrac{6.34}{59.83}\right)\right)}{\ln\,(1-0.0795)} = 0.890$$

$$R_{S,2} = 0.890 * 100\% = 89.0\%$$

Appendix 5.3 – Full Results of Retentions for BPA and Salts

Note – Note for solutions with no NaCl concentration present, salt retention refers to the retention of the small quantity of natural salts present in the water used to make the solutions.

Table 9.7: NP030 Retention Results

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	BPA Retention (%)	Salt Retention (%)	Volumetric Flux (m^3/m^2s)
4	6	1	0	0	12.0%	77.9%	4.57283E-06
8	6	1	0	0	-4.1%	73.7%	7.44827E-06
4	6	1	1	0	31.6%	71.9%	3.91627E-06
8	6	1	1	0	18.5%	85.9%	6.43079E-06
4	6	1	1	1000	22.5%	8.9%	4.16369E-06
8	6	1	1	1000	9.6%	22.5%	6.37114E-06
4	6	1	1	2000	5.5%	13.1%	4.15767E-06
8	6	1	1	2000	6.4%	21.5%	6.78027E-06
4	8	1	0	0	-10.1%	77.8%	3.49566E-06
8	8	1	0	0	22.8%	90.8%	6.31937E-06
4	8	1	1	0	22.4%	68.6%	3.39245E-06
8	8	1	1	0	-0.9%	88.8%	6.07303E-06
4	8	1	1	1000	40.9%	17.9%	3.42384E-06
8	8	1	1	1000	16.3%	29.1%	6.08632E-06
4	8	1	1	2000	-44.0%	8.3%	3.24052E-06
8	8	1	1	2000	8.8%	20.1%	5.7849E-06

Table 9.8: NF270 Retention Results

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	BPA Retention (%)	Salt Retention (%)	Volumetric Flux (m^3/m^2s)
4	6	1	0	0	72.3%	89.0%	9.26219E-06
8	6	1	0	0	46.8%	64.8%	1.91413E-05
4	6	1	1	0	69.8%	81.7%	9.14399E-06
8	6	1	1	0	91.4%	83.2%	1.80186E-05
4	6	1	1	1000	68.1%	64.0%	6.96871E-06
8	6	1	1	1000	66.8%	38.4%	1.70824E-05
4	6	1	1	2000	60.3%	46.4%	6.77412E-06
8	6	1	1	2000	71.5%	50.1%	1.34585E-05
4	8	1	0	0	76.3%	88.1%	9.78141E-06
8	8	1	0	0	72.6%	86.7%	1.81779E-05
4	8	1	1	0	52.8%	87.5%	9.55022E-06
8	8	1	1	0	64.2%	85.1%	1.82072E-05
4	8	1	1	1000	58.0%	63.6%	7.92006E-06
8	8	1	1	1000	66.1%	65.1%	1.62574E-05
4	8	1	1	2000	72.9%	54.5%	6.86575E-06
8	8	1	1	2000	71.5%	55.7%	1.43988E-05

The discarded results are also given below.

Table 9.9: Discarded NP030 Retention Results

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	BPA Retention (%)	Salt Retention (%)	Volumetric Flux (m^3/m^2s)
4	6	1	0	0	2.4%	73.5%	4.60705E-06
8	6	1	0	0	-15.9%	64.3%	6.77301E-06
4	6	1	1	0	16.4%	86.2%	3.99937E-06
8	6	1	1	0	5.3%	74.6%	6.61424E-06
4	6	1	1	2000	-12.9%	-4.5%	4.06221E-06
8	6	1	1	2000	-68.6%	14.5%	5.68002E-06

Table 9.10: Discarded NF270 Retention Results

Pressure (bar)	pH	BPA Conc. (mg/L)	Glucose Conc. (mg/L)	NaCl Conc. (mg/L)	BPA Retention (%)	Salt Retention (%)	Volumetric Flux (m^3/m^2s)
8	6	1	0	0	66.6%	88.5%	1.95619E-05
8	8	1	0	0	64.0%	86.1%	1.87982E-05
8	6	1	1	1000	53.4%	63.5%	1.61989E-05