A SUPERSTRUCTURE BASED OPTIMISATION APPROACH FOR REGENERATION REUSE WATER NETWORK WITH A DETAILED NANOFILTRATION MODEL

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Contributions

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Declaration

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Chemical Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

Signature of Candidate

24th day of February year 2022

Abstract

Increasing costs of purchasing freshwater, coupled with environmental sustainability concerns, have necessitated the adoption of innovative strategies for reducing freshwater consumption and effluent water discharge in chemical processes. Regeneration technologies partially purify process wastewater, thereby increasing opportunities for its reuse and recycle. Nanofiltration has emerged as a competitive wastewater regeneration technology. However, the optimal design of nanofiltration networks has not been extensively investigated. This study presents a framework for the optimal design and synthesis of multicontaminant nanofiltration membrane regenerator networks for application in water minimisation problems. The mathematical optimisation technique is developed based on a superstructure containing all system components and streams, incorporating nanofiltration units, pumps and energy recovery devices. A linear black-box approach and a detailed approach using the Spiegler-Kedem model are explored in modelling the nanofiltration, and the steric-hindrance pore model is used to characterise the membrane. The objective of the optimisation is to simultaneously minimise the water consumption and the total annualised cost of the network. Furthermore, the optimal size, configuration, membrane properties and operating conditions of the equipment are determined. The applicability of the model is illustrated using a case study of an integrated pulp and paper plant. The customized, detailed design of the regenerator network increased freshwater savings by 24% when compared to a black-box model, 31% when compared to a detailed model with fixed module specifications and 41% when compared to a reuse-recycle system with no regeneration. Similarly, cost savings of 38%, 35% and 36% respectively were obtained. It was found that detailed models are preferable when compared to the linear black-box approach. It was also found that the customised design of regenerator models significantly increased the opportunity for environmental and cost savings when compared to the use of pre-selected modules.

Dedication

To my family

“Other things may change us, but we start and end with the family.”

(Anthony Brandt)

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Chapter 1
Introduction

1.1 Background

Water is a vital component in many industries. Chemical processes rely on freshwater, either as a raw material or utility, or both. There are, however, increasing concerns on the sustainability of water resources worldwide. It has been estimated that two-thirds of the world's population will experience water scarcity by 2025 (World Wildlife Fund, 2021) and that by 2050, global water requirements will surpass availability by 50% (Hieminga and Witteveen, 2015). The adverse implications of this crisis on industries, communities, and natural ecosystems are already being felt. As a result, water conservation has become important. There is unprecedented financial, legislative, and social pressure on process industries to reduce their freshwater consumption and wastewater disposal.

Water minimization has been identified as a useful strategy for lowering freshwater intake and wastewater production in process industries. The seminal publication in the area was presented by Takoma et al. (1980). Successive research has significantly improved the understanding of water network synthesis problems and explored the inclusion of additional considerations such as multiple processes, multiple contaminants, pre-treatment and regeneration (Jeżowski, 2010). These techniques can be applied to existing plants through retrofitting and can also be incorporated into the design of new plants. In the absence of water minimisation schemes, about 85% to 96% of the water consumed in plant operations is disposed of as wastewater (WWAP, 2017). The use of wastewater minimisation has proven to reduce this percentage, while also reducing the monetary costs and environmental impacts of process plants (Sachidananda and Rahimifard, 2012).

Regeneration is the treatment of wastewater before it is recycled or reused. Methods used for regeneration can be physical, chemical, or biological. Physical membrane-based separation technologies have been acknowledged as a viable method for water treatment and desalination since the 1950s (Cohen and Glater, 2010). Over the years, these methods have continued to gain prominence. This can be attributed to their lower energy demand, lower capital costs and lower utility costs when compared to traditional methods such as distillation, absorption, stripping, and extraction (Nath, 2011).

Nanofiltration (NF) membranes have a wide range of applications, encompassing industries such as water and wastewater treatment (Shahmansouri and Bellona, 2015) food and beverage manufacture (Cassano et al., 2019), pharmaceuticals (Buonomenna and Bae, 2015; Gadipelly et al., 2014), pulp and paper (Beril Gönder et al., 2011; Mänttäri et al., 2006; Rosa and de Pinho, 1995), textiles (Yaseen and Scholz, 2019) and oil refinery (Santos et al., 2016). Their separation properties overlap those of reverse osmosis (RO) and ultrafiltration (UF), resulting in a wide separation range (Mohammad et al., 2004). When compared, to RO, NF processes tend to have lower energy costs due to lower operating pressures. This makes them economically lucrative in certain cases (Jye and Ismail, 2017). The NF technology is also superior to RO in the treatment of potable water since it retains some trace minerals which are beneficial for human consumption. The lost minerals would need to be re-introduced in the case of RO (Bi et al., 2016). From 2014 to 2019, the global NF market's compound annual growth rate was 15.6%, reaching a total market value of about 445 million United States Dollars (Schäfer and Fane, 2021). By 2023, the market value is expected to have reached about 813 million dollars (Cassano et al., 2019).

Whilst there have been many studies investigating the application of NF in water treatment, the incorporation of NF into the optimisation of water networks has not been studied extensively.

1.2 Motivation

Two approaches have been used to represent water regeneration technologies in water network synthesis problems. The "black-box" (BB) approach is a simplified method, employing linear relations that use a fixed removal ratio (RR) or fixed outlet concentrations to represent the regenerator. The "detailed" approach incorporates complex separation equations, usually resulting in a nonlinear program (NLP) or mixed integer nonlinear program (MINLP). The main advantage of the BB approach is its simplicity. BB models require fewer input data and are less computationally expensive than their detailed counterparts. However, this simplification is also a drawback because the resultant configurations are normally a less accurate representation of how the water network would perform practically

(Nezungai, 2016). The discrepancy between the assumed performance and actual performance can result in high costing inaccuracies, limiting the applicability of BB models (Yang et al., 2014). Detailed regenerator models are advantageous because they provide a more realistic representation of the water network. They also allow for the specification and comparison of different regeneration types. This aids the determination of the most optimal process, or combination of processes when choosing from a variety of options.

NF has emerged as a competitive water regeneration process. There have been many investigations on NF application in treating various types of wastewater, as well as its transport mechanisms (Agboola et al., 2015; Hilal et al., 2004; Mohammad et al., 2015). However, very few studies have explored the incorporation of NF regenerators into the optimal design and cost estimation of water networks. To the best of the survey of literature carried out, it was found that there is currently no model that incorporates a detailed nanofiltration model while simultaneously performing the design of a water network and nanofiltration regenerator network, accounting for all possible configurations of equipment, incorporating a pumping network and exploring opportunities for energy recovery.

In the broader spectrum of pressure-driven membrane-based separation (NF, RO, UF, etc.), previous studies incorporating these methods into the superstructure-based optimal design of water networks have used specified, commercially available membrane modules with known characteristics. The optimisation was thus performed under the implicit assumption that the predetermined module was the best for the system. Whilst available heuristics and manufacturer guidelines are useful in selecting the correct size of modules for water networks, much benefit can be derived from a mathematical framework that selects the optimal characteristics of the membrane module based on the requirements of the system. The results can be applied in selecting the most suitable membranes and modules from commercially available options, or in the fabrication of custom-made membranes and modules for specific water networks and contaminants.

This dissertation aims to address the aforementioned gaps by using superstructure-based mathematical optimisation techniques to synthesise a water network containing a detailed NF regenerator network, whose module properties are determined by the model based on the water quality and process requirements. The research can find application in various sectors such as water desalination, dairy, petrochemical, mining, textile and pulp and paper industries.

1.3 Research Objectives

The objective of this research is to develop a standalone NF regenerator model, capable of designing customised regenerator modules and incorporating a pumping network, and thereafter apply the model in the minimisation of freshwater consumption and wastewater discharge for a water network.

1.4 Problem Statement

The problem statement is formulated as follows:

Given:

i. A set, I, of wastewater generating sources, $i \epsilon I$, with known flowrates, F_i, containing a set, M, of solutes, $m \epsilon M$, with known concentrations, $C_{i,m}$
ii. A freshwater source, with a variable flow rate;
iii. A set, J, of water-using streams $j \epsilon J$ with known minimum allowable flow rates, F_j^L, and maximum allowable concentration of each undesired solute in this lean stream, $C_{j,m}^U$;
iv. A wastewater stream, with a variable flowrate and known maximum allowable contaminant concentrations $C_m^{WW^U}$ based on environmental constraints.
v. Ranges of nanofiltration module design and operational parameters based on data obtained from manufacturers;
vi. Costing parameters such as membrane costing factor, electricity costing factor, annual operating time, membrane life span;

it is desired to obtain the optimum water network and regenerator network which minimises the amount of freshwater consumed, and wastewater disposed of, as well as the total annualised cost of the water network.

1.5 Dissertation Structure

The remainder of this dissertation is structured as follows:

Chapter 2 contains a literature review, outlining wastewater minimisation theory, progress made in the area, current challenges, and opportunities for future research.

Chapter 3 gives a detailed description of the model formulation. In **Chapter 4,** the model is applied to an illustrative example from literature, and the results obtained are discussed. **Chapter 5** contains a summary of the work, highlighting key findings and opportunities for further research.

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Chapter 2
Literature Review

Process integration is a holistic design approach that emphasises the simultaneous design and optimisation of entire processes instead of designing and optimising individual units separately (El-Halwagi and Yee Foo, 2014). For over four decades, Water network synthesis (WNS) has been a key subject area in process integration. The research field plays a significant role in addressing water scarcity concerns and the increasingly stringent regulations enforced on industries regarding the procurement of freshwater and disposal of wastewater.

This chapter contains a review of literature in the area of WNS, with emphasis on systems containing regeneration. The first sections provide a background of the field and the techniques used to synthesise water networks. This is followed by a comprehensive review of WNS schemes containing regeneration and an overview of the available regeneration methods. Finally, a description of the nanofiltration process and models that have been used to describe it are provided.

2.1 Water Network Synthesis (WNS)

Water minimisation is the reduction of freshwater consumption and wastewater generation through water reuse, recycle and regeneration (Y. P. Wang and Smith, 1994). Figure 2-1 illustrates the differences between these three processes. Reuse is when wastewater from a process operation is used in other operations, with exception of the process where it was originally used. In recycling, water is returned to the process in which it was originally used. Regeneration reuse and regeneration recycle involve the partial treatment of water before it is recycled or reused. The purpose of regeneration is to lower the concentration of contaminants in the wastewater, thereby creating more opportunities for the water to be reused or recycled.

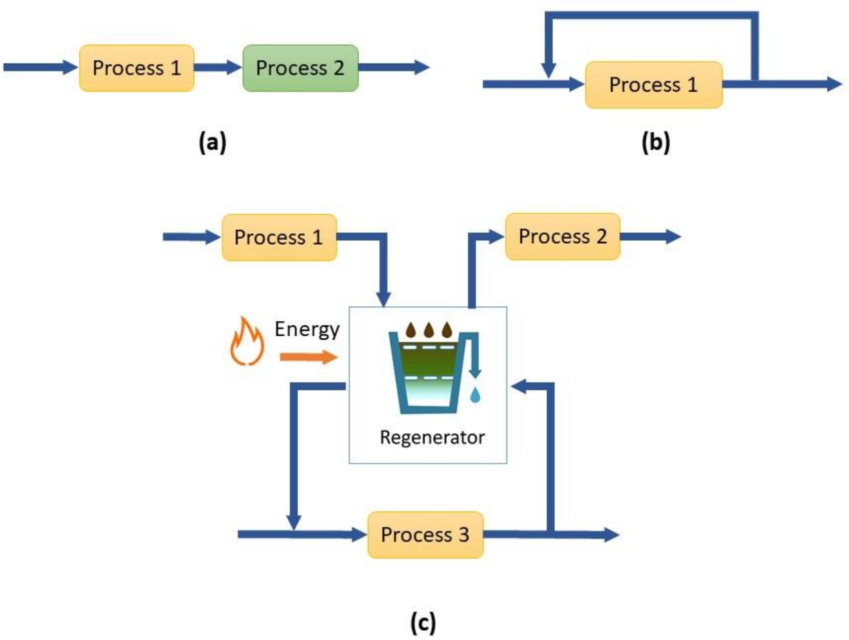

Figure 2-1:(a) Reuse of water from process 1 in process 2 (b) Recycle of water from process 1 (c) Regeneration reuse from process 1 to 2 and regeneration recycle in process 3

The first step in water minimisation is formulating a water network (WN). WNs typically contain water sources, water-using processes (sinks), wastewater disposal sites and water treating processes (regenerators). The streams entering and exiting these components are interlinked using mixers and splitters. The contaminant concentration in sources is usually known, although it is variable for sinks, normally constrained by the maximum concentration at which the water using process can operate. For wastewater disposal sites, the contaminant concentration also tends to be variable, although it must fall within known environmental disposal limits. It is also common to assume a fixed amount of available freshwater sources, with a known unit freshwater cost.

Takama et al. (1980) pioneered the study of the WNS problem. They developed a superstructure based linear programming method to determine an optimal WN which minimised the cost of freshwater and wastewater treatment in a petroleum refinery. The network contained both water-using and water-treating processes. This type of system is known as a total WN (TWN). The field of WNS has now expanded to encompass areas such as multiple contaminant systems (Y. P. Wang and Smith, 1994), batch facilities (Almató et al., 1997), eco-industrial parks (Lovelady and El-Halwagi, 2009), interplant water networks (Alwi et al., 2011), networks with uncertainties (Khor et al., 2014), networks containing pre-treatment (Ng et al., 2009), heat integrated WNs (Savulescu et al., 2005), domestic greywater reuse (Khor et al., 2020), networks containing internal water mains (Cao et al., 2004), networks with regeneration (Kuo and Smith, 1998a), as well as the valorisation of regenerator wastes (Misrol et al., 2021). Various approaches have been applied in the solution of WNS problems. These can be classified into graphical methods, algebraic methods and mathematical optimisation techniques. Hybrid methods, comprising combinations of these approaches, have also been used.

2.2 Graphical Methods for WNS

Graphical methods have been applied to the synthesis of hydrogen distribution systems (Alves and Towler, 2002), utility gas networks (Foo and Manan, 2006), carbon-constrained power system planning (Tan and Foo, 2007), WNs (Y. P. Wang and Smith, 1994) and other types of systems. Water pinch analysis (WPA) is the most common graphical method of WNS. In this method, minimum freshwater flow rates for the WN are targeted by constructing a graph known as the composite curve. After finding the target flow rates, the network is designed based on demand and supply, taking into account the restrictions imposed by the contaminant concentrations in each stream (Foo, 2009).

Wang and Smith (1994) developed the first pinch WN. The basis of this technique was the general approach presented by El-Halwagi and Manousiouthakis (1989) for mass exchange network synthesis. In 1999, Sorin and Bédard formulated the evolutionary table method to estimate the freshwater target. Hallale (2002) proposed the use of the water surplus diagram for the same purpose. This was an adaptation from hydrogen network analysis (Alves and Towler, 2002). Although these methods obtained good pinch points, they were tedious.

2.3 Algebraic Methods for WNS

Graphical methods are very useful for providing insights at the grassroots stages of a design, but algebraic methods are more efficient and easier to interface with other software such as process simulators and spreadsheet applications (Foo, 2016).

Water cascade analysis (WCA) is an algebraic method, introduced by Manan et al. (2004). It replaced the time-consuming steps graphical steps in WPA with a more efficient tabular numerical method. In 2003, El-Halwagi et al. proposed another graphical method known as the Material Recovery Pinch Diagram. This was a more rigorous and systematic approach, which yielded more accurate targets when compared to previous approaches. In 2007, Almutlaq and El-Halwagi proposed the algebraic targeting approach. Like WCA, this method is tabular. However, a key distinction between the two methods is their basis. The algebraic targeting approach is based on the material recovery pinch diagram, whereas WCA is based on material surplus (Foo, 2009).

2.4 Mathematical Optimisation Methods for WNS

While graphical and algebraic methods are very useful in target-setting before performing a detailed design, they are not well-suited for very complex WNS problems such as those with many contaminants, sinks, sources or regenerators (Kuo and Smith, 1997). Another drawback is they mainly focus on the flow rate and contaminant concentration, and cannot easily incorporate other important factors such as economic, geographical and safety constraints. Thus, a holistically beneficial solution is seldom guaranteed. (Doyle & Smith, 1997). Mathematical optimisation techniques address these limitations by enabling a more robust and rigorous approach to the solution procedure, allowing for the inclusion of more detail. Mathematical optimisation is therefore more preferable in cases with complications such as multiple contaminants, sink-source interactions, variations in operational temperatures (Lee et al., 2020), and many uncertainties (Karuppiah and Grossmann, 2007). Mathematical programming also allows for the conduction of sensitivity analyses, where the correlation between the objective and a parameter is investigated by varying the parameter (Budak Duhbacı et al., 2021). A drawback of mathematical techniques is that they usually are computationally expensive, particularly when they involve nonconvexity and nonlinearity. This leads to large requirements on time, computer memory and computational power (Abass and Majozi, 2016).

Mathematical optimisation translates practical problems into a system of mathematical equations, known as a model. In process integration, the initial step in mathematical optimisation is generating a superstructure. A superstructure is a network in which all the possible solutions are embedded. The optimal solution is thus always a subset of the superstructure. A WNS superstructure contains all streams and equipment that can be included in the WN, and all possible connections between them (Jeżowski, 2010). The optimisation model is formulated based on the superstructure. To obtain a good model, it is necessary to have a clear understanding of the problem being investigated. This involves making an analysis of the information that is available (given) and determining the question or questions that need to be addressed (objective function/s) (Hartono, 2020). During this formative stage, assumptions are often needed to narrow down the problem, making it more manageable. An assumption may be formed by purposefully suppressing or disregarding considerably immaterial details (Seino, 2005), or by accepting certain details as facts without ample proof (Oxford dictionary of English, 2010). Because erroneous assumptions distort the problem, the quality of the outcome of a mathematical optimisation exercise is largely dependent on the accuracy of the assumptions made (Seino, 2005).

The formulation of a mathematical optimisation model is generally structured as follows:

Given specifications

Minimise or maximise an objective function: $f(x)$ (2.1)

Subject to inequality constraints: $g(x) \leq 0$

and equality constraints: $g(x) = 0$

Parameters and variables are the specified and measurable characteristics of the system to be optimised. The numerical values for parameters are fixed, whereas those for variables are subject to change. These values can be discrete or continuous. Constraints are equations that govern the relationships between certain parameters and variables and those that define the restrictions or limitations on the allowable values of the decision variables (Davis et al., 1986). In a water minimisation scheme, typical parameters include the source and sink flowrates, process specifications and costing factors. Variables can be discrete, in the form of binary selection variables or integers specifying the amount of equipment required. They can also be continuous, as is normally the case with flowrates, concentrations, and costs. Some examples of constraints are mass balance equations, equipment design equations, operating limits for equipment and concentration limits for sinks and the wastewater stream. The objective function is the mathematical expression whose value is to be minimised or maximised. Some of the objectives that can be targeted in WNS problems are the minimum water consumption (Azmi et al., 2020), the minimum annualised cost (Takama et al., 1980) and the maximum profit derived from the operation (Misrol et al., 2021). Depending on the constraints involved, the resultant formulation can be a linear program (LP), nonlinear program (NLP), mixed integer nonlinear program (MINLP) or mixed integer linear program (MILP). WNS programs usually take the form of NLPs or MINLPs (Edgar et al., 2001).

An NLP is a program in which the objective function and/or constraints contain nonlinear terms (Hendrix and G. -Tóth, 2010). A common source of nonlinearity in WNS programs is the bilinear terms that are usually found in the contaminant mass balances for streams obtained by mixing different streams with different concentrations. An example is shown in Equation 2.2. The flowrate of contaminant $m \in M$ going to sink $j \in J$ is the sum of the flowrate of the same contaminant that comes from each source $i \in I$ and from the permeate and retentate streams from each regenerator stage $q \in Q$. These flowrates are calculated by multiplying the total stream flowrate by the concentration of *m* in the stream. With exception of the concentration of *m* in the sources, $C_{i,m}$, all terms in the Equation are variables.

$$f_j c_{j,m} = \sum_{i=1}^{I} f_{i,j} \, C_{i,m} + \sum_{q=1}^{Q} {f^P}_{q,j} {c^P}_{q,m} \sum_{q=1}^{Q} {f^R}_{q,j} \mathrm{c}_{q,m} \qquad \forall j \in J \; \forall m \in M \qquad (2.2)$$

The use of detailed formulations for regeneration, costing, etc. can exacerbate the nonlinearity of a WNS model. For example, this study incorporates the Spiegler-Kedem model (SKM) for nanofiltration. In the SKM, the removal ratio $rr_{q,m}$ is calculated using Equation 2.3. The dimensionless variable $\kappa_{q,m}$ is determined using the exponential Equation 2.4, where $\sigma_{q,m}$, jv_q and $\beta_{q,m}$ are all variables.

$$rr_{q,m} = \frac{\sigma_{q,m}(1 - \sigma_{q,m}\,\kappa_{q,m})}{1 - \sigma_{q,m}\,\kappa_{q,m}} \qquad \forall q \in Q;\ \forall m \in M \tag{2.3}$$

$$\kappa_{q,m} = \exp -jv_q\left(\frac{1 - \sigma_{q,m}}{\beta_{q,m}}\right) \qquad \forall q \in Q;\ \forall m \in M \tag{2.4}$$

MINLPs are NLPs that contain discrete variables. In WNS, MINLPs usually arise from binary decision variables for the existence of equipment, and integer variables quantifying equipment, the number of labourers or other discrete properties of the system. Examples are shown in Equations 2.5 and 2.6 respectively. In Equation 2.5, x_{np} is a decision variable for the existence of a pump at pumping node $np \in NP$. The pump can only exist if the value of the product of the flowrate through the node, f_{np}, and the pressure difference across the node, $p^{out}{}_{np} - p^{in}{}_{np}$, is greater than a specified lower limit, E^L and upper limit E^U. If these conditions are satisfied, the binary variable x_{np} assumes a value of one. Otherwise, it is zero. In Equation 2.6, n_q is an integer variable that represents the number of modules in regenerator stage Q, n_q. This variable is a function of the permeate flowrate from that stage, $f^p{}_q$, the membrane's permeate flux, jv_q, and the area per membrane module, s_q.

$$E^{L}x_{np} \geq f_{np}({p^{out}}_{np} - {p^{in}}_{np}) \geq E^{U}x_{np} \qquad \forall np \in NP \text{ (2.5)}$$

$$n_q = \frac{{f^p}_q}{{jv}_q\, s_q} \qquad \forall q \in Q \text{ (2.6)}$$

Optimal solutions obtained for NLPs and MINLPs can either be global or local optima. A local optimum is optimal within its 'neighbourhood', whereas the global optimum is optimal for the entire feasible region (Zabinsky, 2013). This difference is illustrated in Figure 2 2. Points A and C are local minima for neighbourhoods 1 and 3 respectively because they are the feasible points with the lowest objective function within those regions. Neither of them, however, is the global minimum since they are not the lowest points in the feasible region. Point B is a local minimum for region 2 and it is also the global minimum because no other point in the feasible region, whether in its neighbourhood or other neighbourhoods, has a lower objective function.

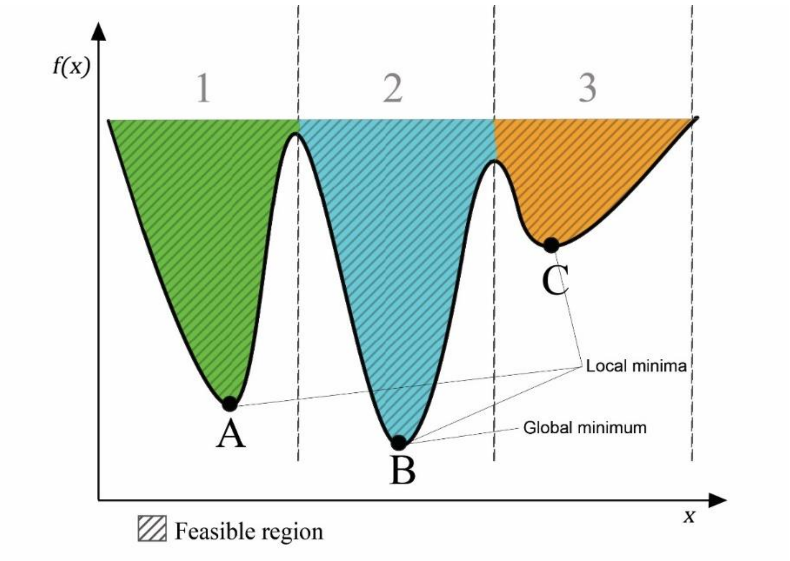

Figure 2-2: Local minima vs. the global minimum

2.4.1 Nonconvexity in WNS Problems

NLPs can be further classified as convex or nonconvex. For an optimisation problem, the three conditions for convexity are (Hendrix and G. -Tóth, 2010):

i. The objective function f and the constraints g_i are differentiable, a stationary point is also a minimum point.
ii. Any local minimum is also a global minimum.
iii. A maximum, known as an extreme point is located at the boundary of the feasible region

Figure 2-3 shows an example of a convex NLP. Any segment connecting any two points that are in the feasible region of a convex NLP will also be within the feasible region. This is not the case for nonconvex NLPs, although convex regions may exist within the feasible region of nonconvex NLPs.

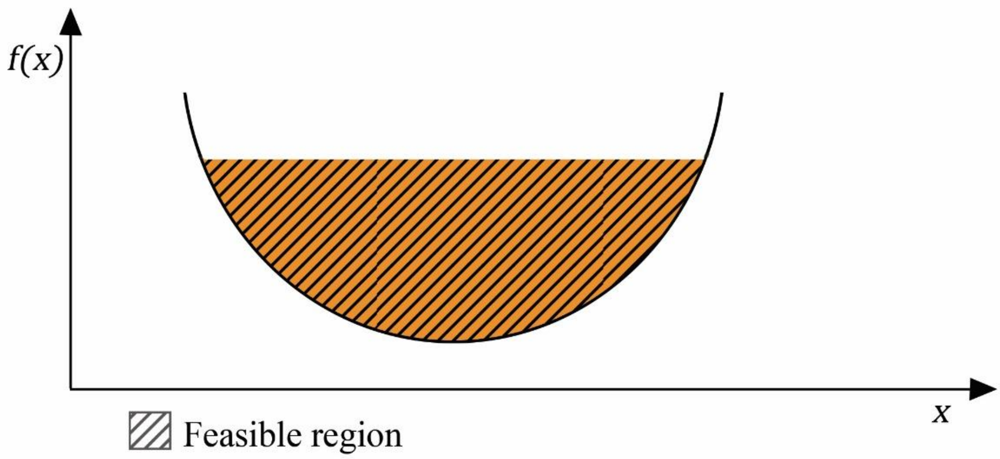

Figure 2-3: Convex NLP

For continuous NLPs, nonconvexity can be due to a nonconvex objective function with multiple local optima, as is the case for Figure 2-4. This type of objective function is known as a multi-modal objective, and it makes it very difficult for the global optimum to be found using conventional NLP approaches. In other cases, the objective function may be convex, but the search space is nonconvex due to the presence of nonconvexity in the constraints. An example is shown in Figure 2-5 (Tawarmalani and Sahinidis, 2005).

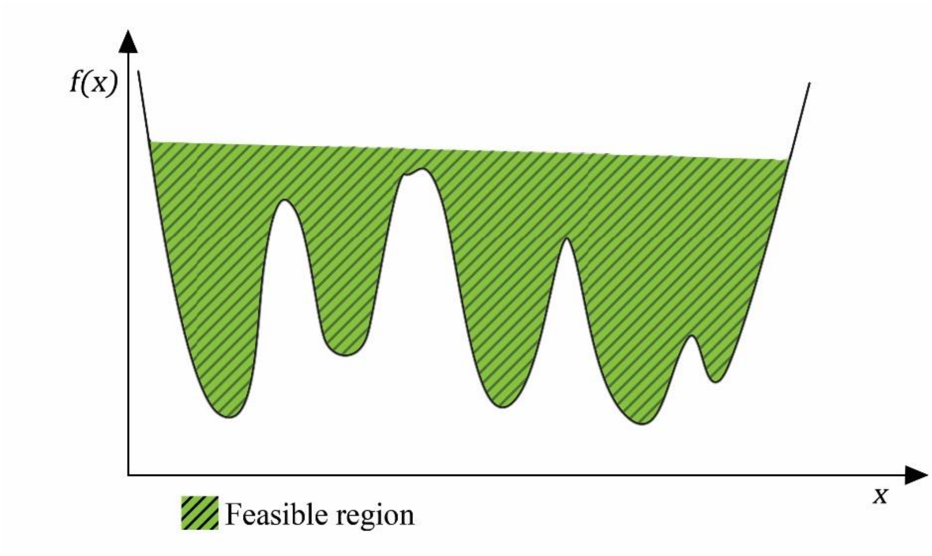

Figure 2-4:Nonconvexity due to multimodal objective

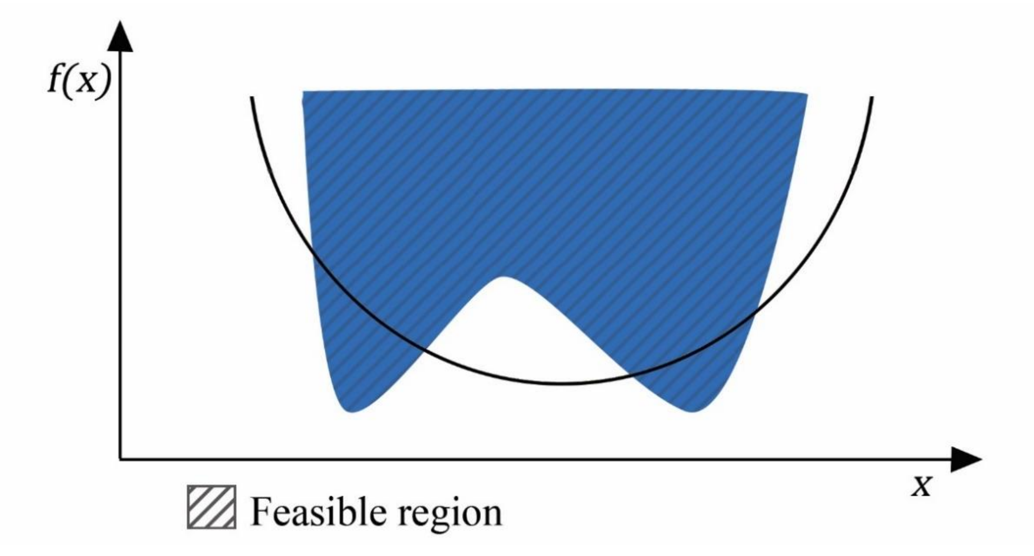

Figure 2-5: Nonconvexity due to a nonconvex feasible region

By the definition of convexity, MINLPs are inherently nonconvex since their feasible regions are discrete as shown in Figure 2-6. In practice, however, MINLPs are only considered nonconvex if a continuous relaxation does not result in a convex NLP. Continuous relaxation entails disregarding the integer requirements of the program (Kronqvist and Lundell, 2019).

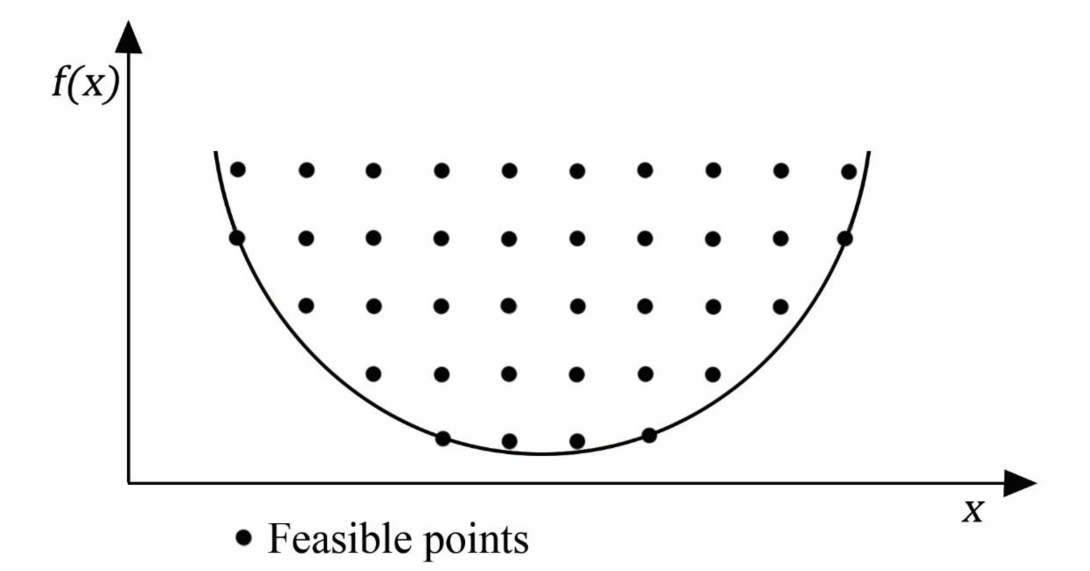

Figure 2-6:Nonconvexity due to integral variables

Convexification is the process of converting a nonconvex program into a convex program. This area of study was necessitated by the complexity imposed by nonconvexity, as well as the inability to guarantee a global optimum when using most of the available NLP solution algorithms and solvers on programs containing nonconvexity (Grossmann, 2002). Two commonly used convexification techniques are the Glover transformation (Glover, 1975) and the McCormick relaxations (McCormick, 1976).

2.4.2 MINLP Solution Algorithms and Solvers

Various algorithms have been proposed for solving MINLP problems. These can broadly be classified into two categories: deterministic methods and stochastic methods. In deterministic algorithms, the solution obtained for an optimisation problem is completely determined by the initial conditions and parameters set at the beginning. There is no randomness, so a set of inputs will always produce the same set of outputs for the same problem (Renard et al., 2013). Deterministic MINLP algorithms include the branch and bound method (Dakin, 1965; Gupta and Ravindran, 1985), the extended cutting plane method (Westerlund and Pettersson, 1995), extended supporting hyperplane (Kronqvist et al., 2016), generalised benders decomposition (Geoffrion, 1972) and outer approximation (OA) (Duran and Grossmann, 1986).

Stochastic algorithms are inherently random. They contain some random variable or distributions, therefore a unique solution cannot be guaranteed every time optimisation is performed using the same input (Renard et al., 2013). When compared to deterministic methods, stochastic methods make it easier to solve complex problems, which may fail to converge using deterministic techniques. However global optimality cannot be guaranteed (Francisco et al., 2005). Some examples of stochastic methods are random search algorithms (Zabinsky, 2009), genetic algorithms (Holland, 1975), clustering algorithms (Xu and Tian, 2015) and simulated annealing (Kirkpatrick et al., 1983).

Solvers are software that use algorithms to find solutions to mathematical problems. Whilst also available individually, MINLP solvers are usually connected to modelling environments like the Advance Interactive Multidimensional Modelling System (AIMMS), A Mathematical Programming Language (AMPL), the GAMS General Algebraic Modelling System, and more recently, Pyomo in Python and JuMP in Julia (Bernal et al., 2018). The Network-Enabled Optimization System (NEOS) server (Czyzyk et al., 1998) is a free online platform hosted by the Wisconsin Institute for Discovery. It allows users to upload a problem, which is solved remotely using a solver of the user's choice, and the solution is returned to them afterwards. Table 2-1 summarises some of the popular MINLP solvers, the algorithms they use and the platforms they are available on.

Table 2-1: MINLP solvers

Solver	Reference	Algorithms used	Licence type and platforms
Alpha Extended Cutting Plane (AlphaECP)	(Westerlund and Pörn, 2002)	○ Alpha Extended Cutting Plane	Commercial licence ○ GAMS ○ NEOS
Algorithms for coNTinuous / Integer Global Optimization of Nonlinear Equations (ANTIGONE)	(Misener and Floudas, 2014)	○ Branch and cut	Commercial licence. ○ GAMS ○ NEOS
AIMMS Outer Approximation (AOA)	(Hunting, 2011)	○ Outer approximation	Commercial licence (customisable source code) ○ AIMMS

Branch and Reduce Optimization Navigator (BARON)	(Ryoo and Sahinidis, 1996)	○ Branch and bound	Commercial licence. ○ Standalone ○ AIMMS, ○ AMPL ○ GAMS ○ JuMP ○ MATLAB ○ NEOS ○ Pyomo, ○ YALMIP
Basic Open-source Nonlinear Mixed Integer Programming (BONMIN)	(Bonami et al., 2008)	○ Branch and bound ○ OA based branch and cut	Open source ○ Standalone ○ AMPL ○ C++ ○ GAMS ○ JuMP, ○ MATLAB ○ NEOS ○ Pyomo ○ YALMIP
Convex Over and Under Envelopes for Nonlinear Estimation (Couenne)	(Belotti et al., 2009)	○ Branch and bound	Open-source ○ Standalone ○ AMPL ○ C++ ○ GAMS ○ JuMP ○ NEOS ○ OS ○ Pyomo
Discrete Continuous Optimizer (DICOPT)	(Grossmann et al., 2002)	○ Outer approximation	Commercial licence. ○ GAMS ○ NEOS

Jump Non linear Integer Program solver (Juniper)	(Kröger et al., 2018)	○ Branch and bound	Open-source ○ JuMP
Knitro	(Byrd et al., 2006)	○ Branch and bound	Commercial licence. ○ AIMMS, ○ AMPL ○ C++ ○ C# ○ Fortran ○ GAMS ○ Java ○ JuMP ○ NEOS ○ Pyomo
Linear, Interactive, and Discrete Optimizer (LINDO)		○ Branch and cut	○ C ○ C++ ○ Delphi ○ Excel ○ Fortran ○ Java ○ JuMP ○ GAMS ○ LINGO ○ MATLAB ○ NEOS ○ .NET ○ Ox ○ Python ○ R
Mixed-Integer Nonlinear Optimization Toolkit: Algorithms,	(Mahajan et al., 2021)	○ Branch and bound	Open-source ○ Standalone ○ AMPL ○ C++

Underestimators, and Relaxations (MINOTAUR)			
Muriqui	(Melo et al., 2020)	○ Extended cutting plane ○ Extended supporting hyperplane ○ OA ○ Branch and bound	Open-source ○ Standalone ○ AMPL ○ C++
Pavito	(Coey et al., 2020)	○ OA ○ Branch and bound	Open-source ○ JuMP
Simple Branch and Bound (SBB)	(Bussieck and Drud, 2001)	○ Branch and bound	Commercial licence. ○ GAMS ○ NEOS
Solving Constraint Integer Programs (SCIP)	(Achterberg, 2009; Vigerske and Gleixner, 2018)	○ Branch-cut-and-price	Free academic license. Paid commercial licence. ○ Standalone ○ AMPL ○ C ○ GAMS ○ JuMP ○ MATLAB ○ NEOS ○ Java ○ Pyomo

			○ Python
Supporting Hyperplane Optimization Toolkit (SHOT)	(Kronqvist et al., 2016)	○ Extended supporting hyperplane	Open-source ○ Standalone ○ C++ ○ GAMS

2.5 Hybrid methods for WNS

The combination of mathematical and graphical or algebraic WNS methods has also been investigated, aiming to benefit from the strengths of each method whilst mitigating some of the weaknesses by applying the other method(s). In 2008, Oliver et al. optimised the water network for a winery using a combination of WPA and mathematical modelling. Mabitla and Majozi (2019) used the graphical composite table algorithm method, combined with mathematical optimisation, to synthesise a water network containing detailed RO regenerator units. More recently, Quintero et al. (2021) applied the hybrid approach in minimising the freshwater consumption in wastewater obtained from the beneficiation of shrimp shells. A target flow rate was obtained using the contaminant cascade methodology (Chin et al., 2021). Thereafter, superstructure-based mathematical optimisation was applied to minimise the freshwater and total cost of the network. This step incorporated reverse osmosis regenerators with a predetermined removal ratio of 90% for each of the contaminants present. A 40% reduction in freshwater consumption was obtained in the absence of regeneration. The presence of regenerators increased the freshwater savings to 48%.

2.6 Regeneration in WNS

Regeneration is the partial treatment of water from sources before it is reused or recycled to the water using processes in a WN (Kuo and Smith, 1998b). The integration of regenerators into the synthesis and optimisation of WNs further reduces water consumption when compared to only employing direct reuse and recycle (Fan et al., 2018). Regeneration units can either be centralised or distributed. The difference between these two configurations is illustrated using the examples in Figures 2-7 and 2-8. In a centralised system, shown in Figure 2-7, the regenerator feed is mixed before being treated, whereas in a distributed system, shown in Figure 2-8, mixing is not mandatory before treatment, and is only done where necessary. Distributed regenerators are more common since they allow the categorisation of streams, resulting in lower total treatment flow rates and reduced capital and operational costs in comparison to centralised systems (Galan and Grossmann, 1998).

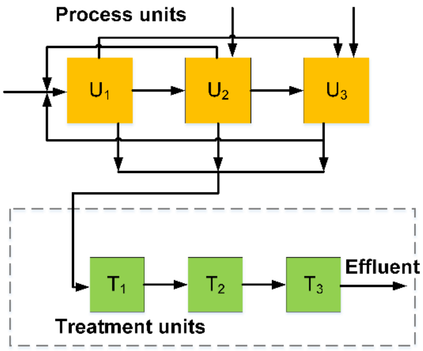

Figure 2-7: Centralised regeneration system

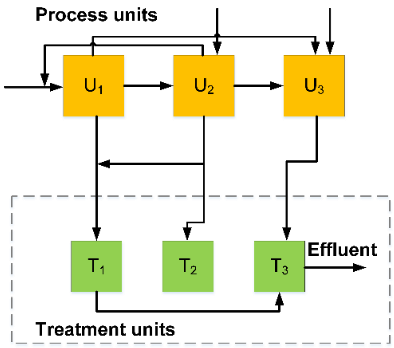

Figure 2-8: Distributed regeneration system

Two approaches have been used to represent water regeneration technologies in WN models. In the traditional black-box (BB) approach the regeneration process is either represented using a fixed contaminant removal ratio or fixed contaminant outlet concentration (Y. P. Wang and Smith, 1994). In such cases, it is not necessary to know the type and design of the regenerator used or its properties and operating parameters. The effect of factors such as contaminant concentrations, process conditions like temperature and pressure and interactions between multiple contaminants on the regeneration process are also not represented. Because of this, using the BB approach may distort the cost of the WN, as the cost of the regenerator may not be calculated accurately since it is only estimated as a function of the flow rate through the regenerator. The inaccuracy caused by BB representation can be as high as 85% (Chew et al., 2008; Nezungai, 2016).

In detailed regenerator models, the removal ratio and outlet concentrations of the regenerator are variable. This is usually done by employing experimentally validated mass transfer models, where the amount of contaminant removed is a function of the design of the regenerator, the operating conditions, and the quality and nature of the regenerated water. Detailed regenerator models are advantageous because they provide a more realistic cost for the WN than BB models. They also allow for the specification and comparison of particular regeneration types (Buabeng-Baidoo and Majozi, 2015). They do, however, require more information on the transport mechanisms of the regeneration process, as well as the operating mechanisms of equipment to be used. This information is not always easy to obtain, and this may be a deterrent. The contaminant removal mechanisms are also often represented by nonconvex, nonlinear equations, making the models computationally expensive, and sometimes impossible to solve. There have been many improvements in the capacity of computers to handle larger and more complex problems. Improved algorithms and solvers have also been developed for nonlinear programs over the years (Kronqvist et al., 2019). Manufacturers' datasheets and pricing catalogues for regeneration equipment are now more easily obtainable from the internet, making it easier to determine their properties and costs.

Table 2-2 contains a synopsis of studies in WNS featuring regeneration. For each publication, the summary of the work, the optimisation objective, solution approach used, freshwater savings attained, and nature of regeneration model used (BB or detailed) are recorded. Where available, the type of regenerator used and freshwater savings obtained in the absence of a regenerator are also cited. It is clear from these studies that the incorporation of regeneration produces significant freshwater savings for WNs, regardless of the nature of the process or the type of regenerator used. Since the objectives of many of the studies were monetary; in the form of minimum cost or maximum profit; it is also evident that incorporating regenerators is also financially beneficial to most WNs.

Table 2-2: Studies containing regenerators

Reference	**Summary**	**Objective**	**Regenerator type**	**Solution technique**	**Model type**	**FW saving (%)**
(Quintero et al., 2021)	Water minimisation in beneficiation of shrimp shell waste.	Min TAC	RO	Hybrid (algebraic+ deterministic)	BB	48

(Lee et al., 2020)	General model for retrofitting WNs	Max TAC saving	DAF	Mathematical (deterministic)	BB	84.5
		Max TAC saving Max FW saving	DAF	Mathematical (deterministic)	BB	56.2
(Misrol et al., 2021)	WN containing domestic and industrial WW, regenerators, and a biogas system	Max Profit	NF, UF, RO	Mathematical (deterministic)	BB	34
(Bazolana and Majozi, 2020)	Simultaneous optimisation of utility consumption and production schedule in batch plants, incorporating ED regenerators	Min profit	ED	Mathematical (deterministic)	DT	41.1
(Khor et al., 2020)	Greywater reuse in water networks for urban water management.	Min TAC	MF, RO	Mathematical (deterministic)	BB	57
(Azmi et al., 2020)	Inter-plant multicontaminant water network synthesis. Centralised regeneration.	Min FW	n/d	Mathematical (deterministic)	BB	47.6
(Chin et al., 2019)	Design of heat integrated water networks using P-graph method	Min FW	n/d	Graphical (P-graph)	BB	82.8

(Ma et al., 2019)	Water, energy and carbon minimisation	Min FW	n/d	Graphical	BB	91.5
(Shen et al., 2019)	Synthesis of HIWN with regeneration. Sequential optimisation for five objective functions	Multiple	Stripping Biological treatment	Mathematical (deterministic)	BB	88.2
(Li and Majozi, 2019)	Insight based method for synthesis of flexible batch water networks	Min FW	n/d	Ranking matrix	-	63.9
(Mabitla and Majozi, 2019)	Combining graphical and mathematical approaches to WNS with regeneration	Min TAC	RO	Hybrid (graphical + mathematical)	DT	75.6
(Oke et al., 2018)	Water minimisation for fracturing water in shale gas exploration	Max profit	MD	Mathematical (deterministic)	DT	22.4
(Koleva et al., 2017)	Partial linearisation and fractional reformulation of MINLP model for WNS	Min TAC	CF, SED, DAF, MMF, MF, UF, NF, RO	Mathematical (deterministic)	GB	46
(Abass and Majozi, 2016)	Multi-regenerator network with detailed regenerator models	Min TAC	RO ED	Mathematical (deterministic)	DT	43.7
(Mafukidze and Majozi, 2016)	Synthesis of water network with multi-stage ED regenerator	Min TAC	ED	Mathematical (deterministic)	DT	12

(Nezungai and Majozi, 2016)	Design of detailed ED regenerator with a background process	Min TAC	ED	Mathematical (deterministic)	DT	38
(Yang et al., 2014)	Water network optimisation using unit-specific shortcut regenerator models	Min TAC	RO IX SED UF AS TFB	Mathematical (deterministic)	GB	67
(Khor et al., 2011)	Water network synthesis with mechanistic RO model	Min TAC	RO	Mathematical (deterministic)	DT	58

AS: Activated sludge, CF: coagulation-flocculation, DAF: dissolved air floatation, ED: electrodialysis, FW: freshwater IX: ion exchange, MD: membrane distillation, MED: multi-effect distillation, MF: microfiltration, MMF: media filtration, NF: nanofiltration, RO: reverse osmosis, SED: sedimentation, TAC: total annualised cost, TFB: trickling filter bed, UF: ultrafiltration, n/d: not disclosed.

Many of the studies shown in Table 2-2 used the BB approach or shortcut models to represent the regenerator. However, there has also been increasing attention on detailed approaches. Khor et al. (2011) incorporated a rigorous nonlinear reverse osmosis network (RON) model based on the work by El-Halwagi (1992) into a WN. When applied to a petroleum refinery case study, a 58% savings in freshwater was obtained compared to a base case with no regeneration. The model determined the optimum number of RO modules and total surface area, the total annualised cost of the RON and the total annualised cost of the WN. A limitation in the model proposed by (Khor et al., 2011) was that it assumed a single regenerator unit with a fixed design, limiting the flexibility of the RO plant. Building on this work, Buabeng-Baidoo and Majozi (2015) proposed a model that simultaneously minimised the cost of freshwater consumption, wastewater generation and regeneration energy. Their RON model also determined the number of RO units, pumps, and turbines and had a variable removal ratio. It applied to both single contaminant and multicontaminant scenarios. The use of multiple regenerators and a variable removal ratio led to a reduction in the TAC.

(Yang et al., 2014) developed a general-purpose model for application in removing total dissolved solids, total suspended solids and organics. The model selects the best available technology through generalised disjunctive programming (GDP). The options considered were reverse osmosis, ion exchange, sedimentation, ultrafiltration, activated sludge treatment and trickling filter bed. Unit-specific shortcut models were used to describe the contaminant removal. These were accompanied by short-cut cost functions for the various treatment units. Due to the short-cut nature of the regeneration models, the approach used by (Yang et al., 2014) is sometimes referred to as a "grey-box" (GB) approach. Other GB formulations include those of Galán and Grossmann (1999) and Faria and Bagajewicz (2009).

Nezungai and Majozi (2016) developed a multicontaminant electrodialysis model, which they embedded in a pulp and paper WN case study. The model simultaneously minimised freshwater consumption, wastewater generation and energy consumption. Abbas and Majozi (2016) proposed a multi-regenerator MINLP network for simultaneous water and energy minimisation. They incorporated detailed RO and ED models into a WN for the simultaneous minimisation of water and energy. By comparing a variable removal ratio to a fixed removal ratio, they found that a more optimal configuration is obtained when the removal ratio is variable. It was also found that detailed regenerator models provide a more accurate cost and performance representation when compared to BB regenerator models. The results obtained when the model was applied to a pulp and paper case study indicated potential freshwater savings of 43.7%, wastewater reduction of 50.9% and a 46% reduction in the total annualised cost of the WN.

2.6.1 Regeneration Technologies

Various water treatment options are available for regenerating water in WNS. These can be broadly classified into three categories as shown in Figure 2-9. Physical methods are the most popular. These include screening, settling and filtration. Chemical methods include chemical precipitation, coagulation, floatation, flocculation, irradiation, and oxidation. Adsorption is sometimes referred to as a physicochemical method since it can either be physical, chemical or both depending on the adsorbent used and its adsorption mechanism for the contaminant. Biological methods involve the degradation of the contaminant by digestion, which can be aerobic or anaerobic (Hendricks, 2011; Makhlouf and Ali, 2021).

The choice of a regeneration technology is a complicated exercise, as many factors need to be considered. These include the type of contaminant(s) to be removed, the quality of water to be treated and the quality of water required by the water-using processes. The treatment technology's costs, reliability and flexibility, as well as its ease of integration with other processes in the network and the sustainability of the technology should also be considered (Logsdon et al., 1999). Sustainability of regeneration processes encompasses many aspects including legal compliance throughout the lifetime of the operation, energy efficiency, limited water wastage, as well as proper management of residual wastes and by-products (Logsdon et al., 1999; Raseman et al., 2017).

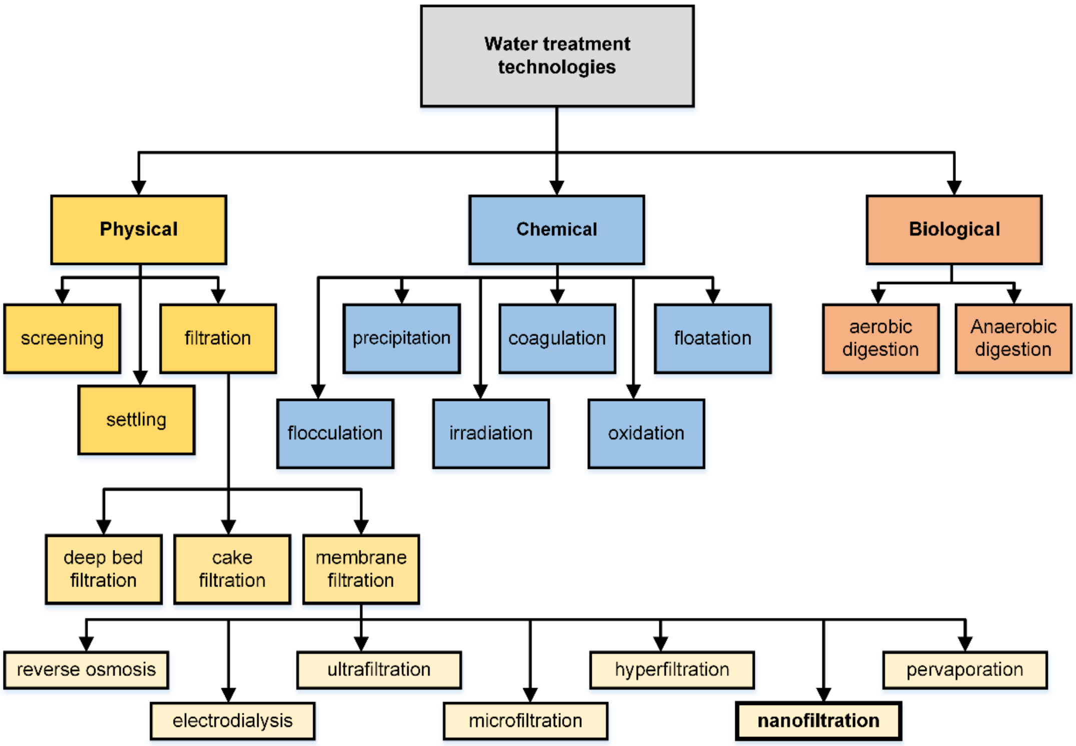

Figure 2-9: Regeneration technologies

Many guides have been published to aid the selection of treatment technologies for water treatment. Some guides only provide theoretical knowledge on the factors to be considered (Logsdon et al., 1999). However, other guides employ logical methodologies to assist in decision making. One such methodology is the multi-criteria decision making (MCDM) framework. This umbrella term encompasses various methods such as the analytic hierarchy process, the analytical network process, the technique for order of preference by similarity to ideal solution method, and the best worst method, which have all been used in selecting treatment methods for various applications (Salamirad et al., 2021).

The formulation of an MCDM problem is shown in Figure 2-10. It is desired to achieve a specified goal, where multiple alternatives are available to do so. Each alternative is assessed based on multiple criteria, and the best alternative is selected. A key characteristic of MDCM techniques is their heavy reliance on the human decision-maker. Unlike automated methods, the human decision-maker provides input and makes choices at various stages of the decision-making process, such that it is unlikely for two decision-makers to obtain the same solution at the end (Ishizaka and Nemery, 2013). Whilst this characteristic is advantageous in making the outcome personalised to the needs of each decision-maker, the results can also be compromised by the subjectivity and error that is usually associated with processes that rely heavily on humans.

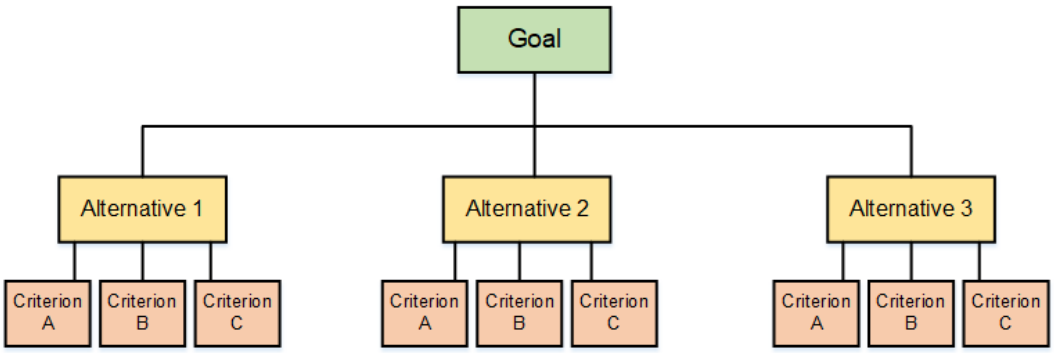

Figure 2-10: Structure of an MCDM problem formulation

In WNS by mathematical optimisation, the choice of regenerator can be embedded into the mathematical formulation. Koleva et al. (2017) considered nine regeneration technologies, arranged in a predetermined sequence based on industry norms. Each technology could be included or excluded from the optimal solution, and multiple passes and stages were allowed for all technologies, within specified limits. The removal ratios for each technology were calculated using GB linear equations based on the concentrations of specific contaminants. The resultant formulation was an MINLP, which could be reformulated into a linearised MINLP or a mixed integer linear fractional program (MILFP). The model was applied to a seawater desalination example and a surface water treatment example. For seawater desalination, five technologies were selected from the nine. The same number of technologies was selected for surface water, although there were differences in the technologies chosen and the stages required for each technology.

Abass and Majozi (2016) considered reverse osmosis and electrodialysis, each with a detailed regeneration model and variable removal ratio calculated using various nonlinear relationships. The technologies could be arranged in any sequence, and any stream could be sent to either or both technologies. A pulp and paper example was used to validate the model. The optimal solution contained both technologies, each receiving input from different streams in the network. Some of the retentate from reverse osmosis was further treated using electrodialysis.

Chauhan et al. (2016) presented a formulation that considered nanofiltration and reverse osmosis for desalination water networks. Any source stream could be sent to either or both of the technologies. The retentate from nanofiltration could be further processed through nanofiltration or reverse osmosis, although the retentate from reverse osmosis could only be reprocessed via reverse osmosis. GB linear relations were used to calculate the removal ratios. The optimal design contained both technologies, with nanofiltration acting as a pre-treatment process for reverse osmosis.

Zhu et al. (2017) developed a formulation containing seven types of regenerators, characterised using unit-specific shortcut models. To avoid overcomplicating the model, the regeneration network was designed using a multi-step approach containing 5 steps. The sources were categorised as either high concentration streams or low concentration streams and directed accordingly. At each step, several regenerator options were available. The formulation was implemented in industrial case studies for coal-based plants. In all cases explored, the optimal network was found to contain a combination of at least three of the available treatment methods.

The findings of these studies imply that ideal regeneration networks for water minimisation will typically contain two or more technologies and that having as many technology options as possible is beneficial when dealing with most types of industrial WNS problems. This, however, does not negate the importance of standalone models where one type of regenerator is studied in detail. Standalone models are a necessary building block towards obtaining efficient multi-regenerator formulations. They have also been proven to be independently effective and may be more practical in some scenarios.

2.6.2 Nanofiltration

Membrane technologies have been applied in the process industry since their inception in the late 1950s (Sirkar, 1997). These technologies include reverse osmosis, electrodialysis, nanofiltration, ultrafiltration, microfiltration, and pervaporation. Their rise in attractiveness can be attributed to their lower energy demand, lower capital costs and lower utility costs when compared to conventional separation technologies like distillation, absorption, stripping and extraction. (El-Halwagi, 1992).

A membrane is a selectively permeable barrier, which allows certain molecules or ions to pass through its pores while blocking others. Membranes can be heterogeneous or homogenous, positively charged, negatively charged, neutral, or bipolar and can exist in both the solid and liquid phases (Ravanchi et al., 2009). Membrane separation depends on the driving force present as well as the molecular size of the components and the physical properties of the membrane. The driving force may be a concentration gradient, electrical potential gradient or hydrostatic pressure gradient (Ravanchi et al., 2009; Strathmann, 1981). Figure 2-11 shows the membrane separation processes, as well as the types of molecules they can remove or retain.

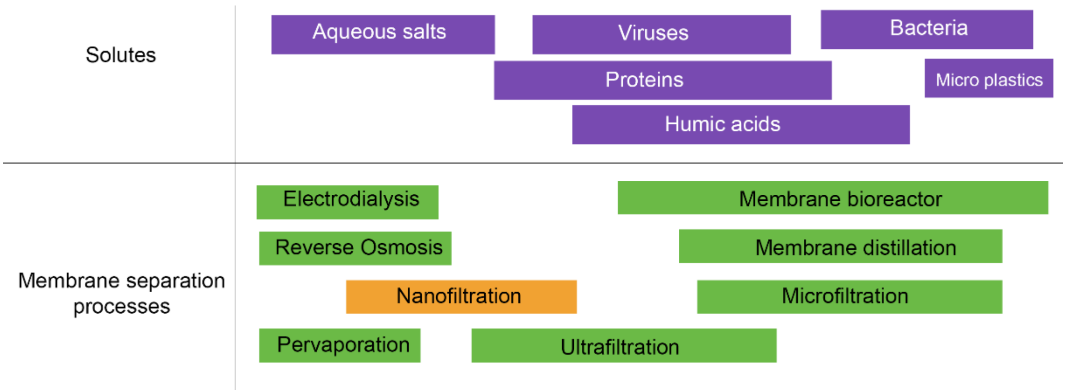

Figure 2-11:Rejection of various solutes by membrane separation processes

NF membranes have a molecular weight cut off (MWCO) of 200-1000 Dalton and pore sizes of 0.1-2.0 nm (Mohammad, 2013). The separation qualities of 'loose' nanofiltration membranes overlap with those of UF, while those of 'tight' membranes overlap with RO. NF fills the gap between the two technologies, allowing for the removal of solutes typically retained in ultrafiltration, as well as the retention of solutes typically removed by reverse osmosis. Figure 2-12 illustrates the separation that occurs during the NF process. The pressure gradient causes solvent ions to pass through the pores of the membrane, together with solute ions whose radius is smaller than that of the pores of the membrane. Steric hindrance, dielectric interactions, and interactions between the solute and the membrane also have an effect, resulting in an imperfect separation. Ions with different charges are also retained differently since the surface of the membrane is charged. Multivalent ions are easily removed, whereas monovalent ions are typically retained unless the pore size is on the 'tighter' end of the spectrum (Schäfer and Fane, 2021).

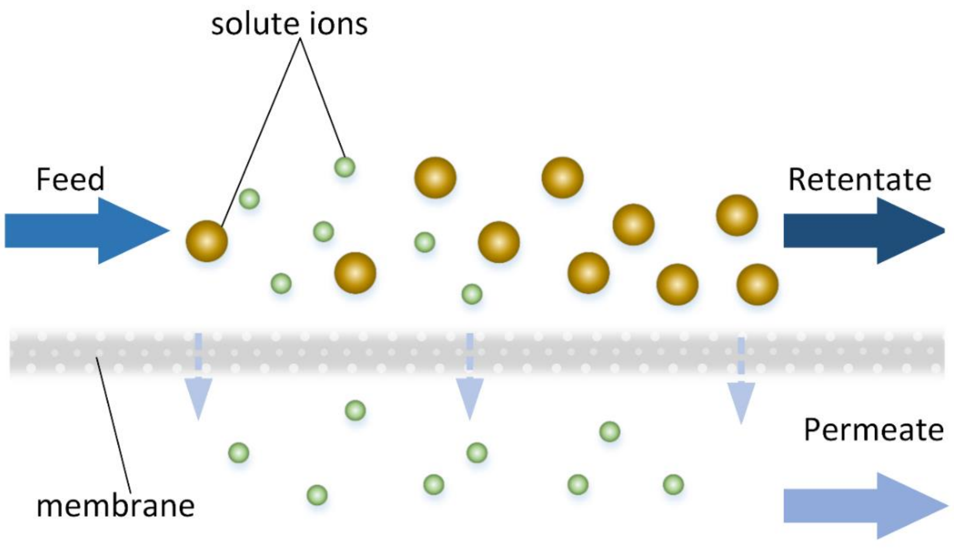

Figure 2-12: Separation using an NF membrane

NF membranes were invented in the 1970s as a solution to the high energy costs associated with the pressure requirements for RO (Van der Bruggen and Vandecasteele, 2003). Since then, the membranes have been applied for various industrial purposes. In the dairy industry, NF is used in whey demineralisation and concentration, and the recovery of lactic acid (Saini et al., 2019). In pharmaceuticals, organic solvent NF has become a pivotal technology for molecular separation (Peeva and Livingston, 2019). NF is also used to remove toxins like amoxycillin from wastewater (Shahtalebi et al., 2011). In the textile industry, NF membranes are used in dye concentration, removal of dye penetrants, concentrating optical brightening agents, and treating wastewater (Synder Filtration, 2021). In beverage manufacture, NF has many applications including the concentration, separation and purification of products such as syrups, alcohol and juices (Cassano et al., 2019).

The desalination and/ or treatment of water is the largest and most widely researched application of NF. This has been largely driven by environmental sustainability and water scarcity concerns. (Oatley-Radcliffe et al., 2017). NF regenerators have been included in water minimisation schemes in the past. However, most of the studies have used the BB or GB models to represent the regeneration process. Tokos and Novak Pintarič (2009) studied the optimisation of a batch water network, containing semi-continuous NF regenerators, for a brewery plant. A BB regeneration model was used. Koleva et al. (2017) developed a formulation for designing water networks containing “fit-for-purpose” treatment systems, where the algorithm selected the regeneration technologies from among those commonly used in industry. These included NF, but a GB approach was used to calculate the removal ratio and regeneration costs were calculated using the regenerator feed flowrate and costing parameters. Misrol et al. (2021) investigated water minimisation and biogas recovery in a scheme containing domestic and industrial wastewater sources. Regeneration could be done through NF, UF or biological digestion. Fixed removal ratios were used for each regenerator. NF regeneration costs were calculated using costing parameters and the flowrates to the regenerator. So far, there is no detailed, standalone comprehensive NF model.

The detailed design of a regeneration network can be conceptualised as a concentric ‘onion’ as shown in Figure 2-13. In NF, the membranes are at the heart of design since they are the means of separating the contaminants from the water streams. These membranes are housed in cylindrical modules, which act as a support and protection for the membrane, while also managing the flow of fluid through the membrane. The regenerator network’s system incorporates the module configuration, auxiliary equipment like pumps and pipes, as well as aspects such as cleaning, pre-treatment and operation controls. These all have a bearing on the overall performance of the regeneration network. The operating concept refers to whether the regeneration will happen in a batch, continuous, or semi-continuous manner (Schäfer and Fane, 2021). This choice is usually dependent on the background processes surrounding the regeneration network. Storage considerations also come into effect when there is a need to hold feed before the regeneration or permeate after the regeneration. Continuous processes usually have continuous regeneration networks, and typically do not require storage. In a few instances such as pilot projects or small plants, batch or semi-continuous regeneration may be preferred (Wadley et al., 1995). For batch processes, the time factor complicates the decisions concerning how the regenerators should be operated and whether storage is required, hence regenerators with background processes that are batch operations should be treated on a case-by-case basis.

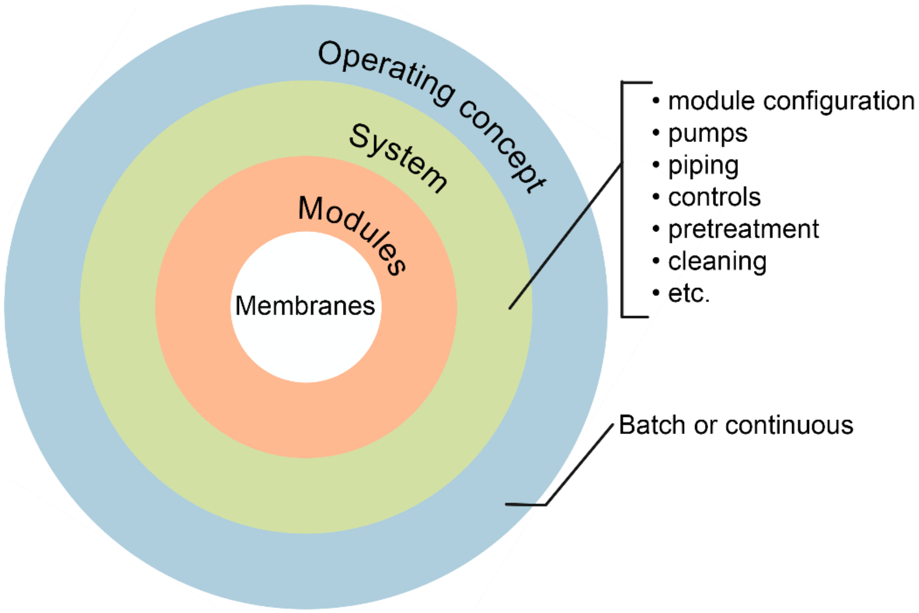

Figure 2-13: Design of an NF regenerator network

2.6.2.1 Nanofiltration Transport Models

Knowledge of the mechanisms governing the transport of the solvent and the solutes through the membrane is important, as it enables the prediction of how a membrane will perform for different solutions (Jye and Ismail, 2017). While these mechanisms are not exhaustively understood, it is known that NF separation is due to sieving effects (also known as steric effects) and electrostatic effects. Of these, the sieving effects are more dominant (Bowen and Mohammad, 1998). As a result, while all nanofiltration transport models account for steric effects, some do not account for electrostatic effects, but have been validated experimentally and are still extensively used in research and design. In the following model descriptions, $m \in M$ is defined to be a solute and $q \in Q$ a nanofiltration module, or stage containing a bundle of modules with the same characteristics.

Spiegler-Kedem Model

The Spiegler-Kedem (S-K) model (Spiegler and Kedem, 1966) is one of the most popular models used for nanofiltration. It is an extension of the Kedem-Kachalsky model (Kedem and Katchalsky, 1963, 1958). Both models are classified as models based on irreversible thermodynamics. Such models describe nanofiltration as an irreversible process, continuously producing entropy and releasing energy. They do not require details about the structure of the membrane, or what occurs within the membrane. This makes the models accessible and practical, especially for use in industrial situations, however, the drawback is that they cannot be independently used to design the membrane (Suárez and Riera, 2016). The S-K model requires three parameters to predict the transport of a solute through the membrane, i.e., the reflection coefficient, solute permeability, and pure water permeability. The conditions assumed in the formulation of the model were:

- Steady-state operation.
- Pressure and concentration differences are the driving force for separation.
- A non-ideal membrane, whose semi-permeability is represented by the reflection coefficient.
- A solution where the volume fraction of the solute (contaminant) is considerably smaller than the volume fraction of the solvent (water).
- Negligible electrostatic interactions between the solute and the membrane.

The permeate flux, jv_q, is calculated using the membrane's solvent permeability and the pressure drop across the membrane, where the osmotic pressure term, $\Delta\pi_q$ is a function of each solute's rejection coefficient. The solute permeability is the flux of solute through the membrane per unit driving force. In the case of nanofiltration, the driving force is the transmembrane pressure difference.

$$jv_q = a_q\left(\Delta p_q - \Delta\pi_q\right) \qquad \forall q \in Q \text{ (2-7)}$$

Where

$$\Delta\pi_q = \mathrm{RT}\sum_{\mathrm{m}=1}^{M} \sigma_{q,m}\left(c^*{}_{q,m} - c^p{}_{q,m}\right) \qquad \forall q \in Q \text{ (1-8)}$$

the removal ratio is calculated using the solute rejection coefficient and a dimensionless variable, $\kappa_{q,m}$, calculated using the reflection coefficient, water flux and solute permeability as shown in Equation 2-10. The solute rejection coefficient, $\sigma_{q,m}$, is defined as a measure of the fraction of the membrane through which the solute will not be transported (Vassilis, 1986). No rejection occurs when $\sigma_{q,m}$ is zero 0 and 100% rejection occurs when $\sigma_{q,m}$ is 1.

$$rr_{q,m} = \frac{\sigma_{q,m}(1 - \sigma_{q,m}\,\kappa_{q,m})}{1 - \sigma_{q,m}\,\kappa_{q,m}} \qquad \forall q \in Q;\ \forall m \in M \text{ (2-9)}$$

$$\kappa_{q,m} = \exp -jv_q\left(\frac{1 - \sigma_{q,m}}{\beta_{q,m}}\right) \qquad \forall q \in Q;\ \forall m \in M \text{ (2-10)}$$

Steric Hindrance Pore Model

Nakao and Kimura (Nakao and Kimura, 1982) proposed the steric hindrance pore (SHP) model, which links the rejection coefficient, to the properties of the membrane and the solute. The reflection coefficient of a solute, *m*, is calculated using the ratio of the solute's radius to the membrane's pore radius, $\lambda_{q,m}$, together with the convection factor, $k^C{}_{q,m}$, which is also a function of $\lambda_{q,m}$.

$$\sigma_{q,m} = 1 - k^C{}_{q,m}\left(1 + \tfrac{16}{9}\lambda_{q,m}{}^2\right) \qquad \forall q \in Q; \forall m \in M \text{ (2-11)}$$

$$\lambda_{q,m} = \frac{rs_m}{rp_q} \qquad \forall q \in Q; \forall m \in M \tag{2-12}$$

$$k^C{}_{q,m} = 2(1-\lambda_{q,m})^2 - (1-\lambda_{q,m})^4 \qquad \forall q \in Q; \forall m \in M \tag{2-13}$$

Each solute's permeability through the membrane is calculated using the solute's diffusivity, D_m, the steric factor for diffusion, $k^D{}_q$, and the ratio of membrane thickness to porosity. $\Delta x/_{\varepsilon_q}$. $k^D{}_{q,m}$ is a function of $\lambda_{q,m}$.

$$\beta_{q,m} = \frac{D_m\, k^D{}_{q,m}}{\Delta x/_{\varepsilon_q}} \qquad \forall q \in Q; \forall m \in M \tag{2-14}$$

$$k^D{}_{q,m} = (1-\lambda_{q,m})^2 \qquad \forall q \in Q; \forall m \in M \tag{2-15}$$

Donnan Steric Pore Model

In addition to steric effects, The Donnan Steric Pore (DSPM) model proposed by Bowen and Mukhtar (1996) incorporates electrostatic effects in the description of the NF separation. Transport of ions through the membrane is governed by the extended Nernst –Planck equation (Schlögl, 1966), Equation 2-16. The first term on the right-hand side of the equation represents transport due to diffusion. The second represents transport due to the electrical potential gradient. The last represents transport due to convection.

$$jv_{q,m} = -D^p{}_m \frac{dc^{mem}{}_{q,m}}{dx_q} - \frac{\zeta_m\, c^{mem}{}_{q,m}\; D^p{}_m}{RT} F \frac{d\psi}{dx_q} + k^C{}_{q,m} c^{mem}{}_{q,m}\, V_q \qquad \forall q \in Q; \forall m \in M \tag{2-16}$$

Where:

$D^p{}_m$ *is the diffusivity of the solute inside the pore*

$c^{mem}{}_{q,m}$ *is the concentration of solute m in the membrane*

ζ_m *is the valence of solute m*

F *is Faraday's constant*

R *is the gas constant*

T *is the temperature*

$d\psi$ *is the potential difference*

dx_q *is the effective membrane thickness*

The diffusivity of the solute inside the pore, $D^p{}_m$, is calculated using the diffusion coefficient and the diffusivity of the solute in the bulk solution.

$$D^p{}_m, = k^d{}_m D_m \qquad \forall q \in Q;\ \forall m \in M \quad (2\text{-}17)$$

The concentration gradient, $\frac{dc^{mem}{}_{q,m}}{dx}$ is calculated as:

$$\frac{dc^{mem}{}_{q,m}}{dx} = \frac{J^v{}_q}{D^p{}_m}\left(K^c{}_m c^{mem}{}_{q,m} - c^p{}_{q,m}\right) - \frac{F\ \zeta_m\ c^{mem}{}_{q,m}}{RT}\frac{d\psi}{dx}_q \qquad \forall q \in Q;\ \forall m \in M \quad (2\text{-}18)$$

The potential gradient, $\frac{d\psi}{dx}_q$, is calculated as:

$$\frac{d\psi}{dx}_q = \frac{\sum_{m=1}^{M}\frac{\zeta_m J^v{}_q}{D^p{}_m}\left(K^c{}_m c^{mem}{}_{q,m} - c^p{}_{q,m}\right)}{\frac{F}{RT}\sum_{m=1}^{M}\left(\ \zeta_m{}^2 c^{mem}{}_{q,m}\right)} \qquad \forall q \in Q; \quad (2\text{-}19)$$

The Donnan - steric partitioning is calculated using:

$$\frac{\gamma_{q,m}\, c^{mem}{}_{q,m}}{\gamma^{mem}{}_{q,m} C_m} = \Phi_m \exp\left(-\frac{F\, \zeta_m}{RT} \Delta\psi_q\right) \qquad \forall q \in Q; \ \forall m \in M \tag{2-20}$$

Where :

$\gamma_{q,m}$ *is the bulk activity coefficient of solute m*

$\gamma^{mem}{}_{q,m}$ *is the activity coeficient of m inside the pore*

$$\Phi_m = (1 - \lambda_m)^2 \qquad \forall q \in Q; \ \forall m \in M \tag{2-21}$$

$$\lambda_{q,m} = \frac{r^s{}_m}{r_{p,q}} \qquad \forall q \in Q; \ \forall m \in M \tag{2-22}$$

2.7 Summary

This chapter has provided background on WNS methods, applications and challenges. Whilst there have been many developments in the area of regeneration, a WNS framework containing a comprehensive, detailed standalone NF model has not yet been developed. This is despite NF being one of the most promising membrane-based regeneration technologies. This work aims to address this gap because such a model will provide insight into the design and optimisation of NF regenerator networks, and also act as a building block in the synthesis of water networks containing multiple types of regenerators.

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Chapter 3

Model Formulation

In this section, a superstructure and an MINLP program encompassing the technical, operational and financial aspects of the regenerator network are formulated using material balance equations, membrane model equations, equipment design equations, operation constraints, environmental constraints and cost equations.

3.1 Superstructure

A superstructure is a diagram representing the network containing all the possible connections and configurations. Consequently, the optimal solution is always a subset of the superstructure. The model superstructure for this research is presented in Figure 3-1. It represents the nanofiltration regenerator network using the state-space approach proposed by El-Halwagi (1992). Feed streams obtained from wastewater generating processes are fed to the pressurisation/depressurisation inlet stream distribution box (PDISDB). A freshwater stream, FW, is available to supplement the regenerator network in supplying feedwater to downstream processes. From the PDISDB, the streams can be distributed to the pressurisation/depressurisation matching box (PDMB) containing pumps and turbines, or directly to the pressurisation/depressurisation outlet stream distribution box (PDOSDB). The PDOSDB sends streams to the nanofiltration stream distribution box (NFSDB), which distributes them to regenerators in the nanofiltration matching box (NFMB) for treatment. Water from the PDOSDB can also be sent to the lean streams for reuse/recycle, and the concentrated waste stream for disposal. Permeate and retentate streams are prohibited from mixing in the PDOSDB to prevent recontamination. The sending of retentate streams to lean outlet streams and permeate streams to the waste stream is prohibited.

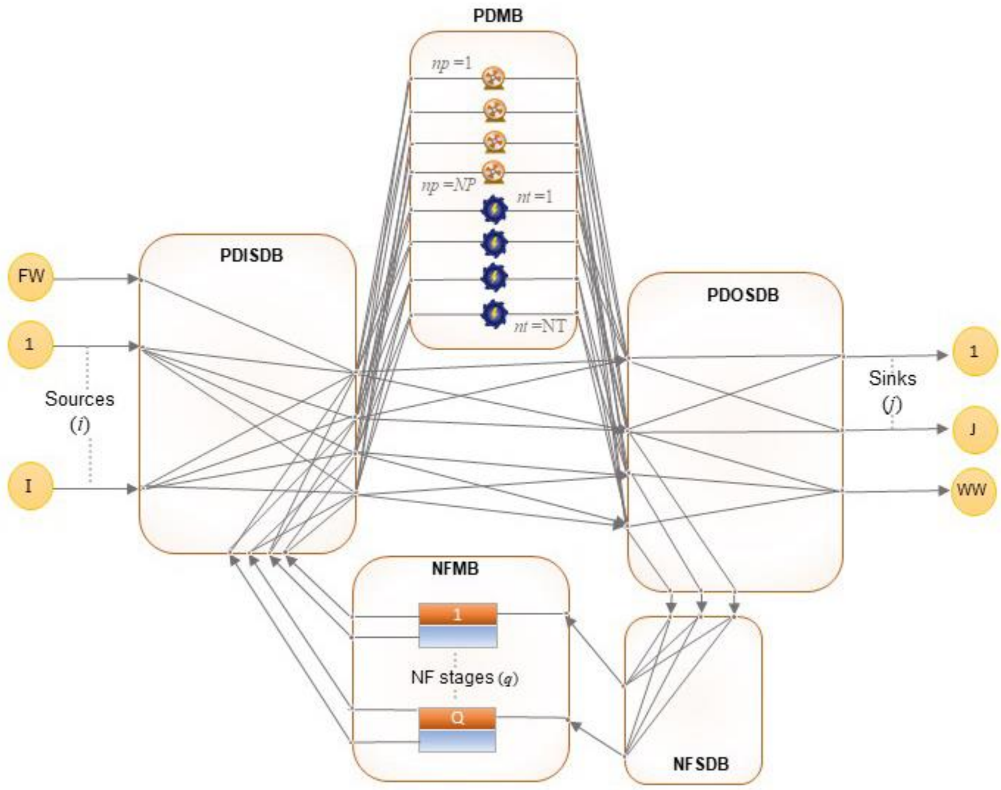

Figure 3-1: Model superstructure

The PDOSDB is an additional feature to the superstructure proposed by (El-Halwagi 1992). It was added to clearly illustrate several scenarios which are possible in the regenerator network:

i. Direct transfer of water from the freshwater stream and feed streams to the outlet lean and streams, provided they meet the concentration requirements of the outlet streams.
ii. Transfer of water to the NFSDB without being pressurised or depressurised, provided they are at the same pressure as the pressure required in the outlet streams.
iii. Transfer of pressurised or depressurised water to the outlet streams without passing through the NFMB again, provided they meet the concentration requirements of the outlet streams.

The superstructure has also been modified to show that a stream in the PDMB can either undergo pressurisation or depressurisation, but not both. This constraint was present in the model formulated by (El-Halwagi 1992). However, it was not explicitly visible on the superstructure. Additionally, the pressurisation and depressurisation nodes previously contained in a common set N have been separated into a set for pumping nodes, NP, and a set of turbine nodes, NT, respectively. This removes ambiguity and negates the need for a constraint that prohibits direct pressurisation after depressurisation and vice versa.

3.2 Material Balances

Material balances are implemented around every unit, mixing point and splitting point to ensure the conservation of mass. In addition to the overall material balance, component balances are also employed to ensure the conservation of mass for each contaminant.

3.2.1 Material Balances for Inlet Streams

Equation 3-1 states that source streams entering the network, F_i, can be distributed to the PDISDB, directly to the waste or lean streams, or directly to the regenerators via the NFSDB.

$$F_i = \sum_{np=1}^{NP} f_{i,np} + \sum_{nt=1}^{NT} f_{i,nt} + \sum_{j=1}^{J} f_{i,j} + f^{WW}{}_i + \sum_{q=1}^{Q} f_{i,q} \qquad \forall i \in I \qquad (3\text{-}1)$$

The flowrate of the freshwater stream is the sum of freshwater going to the lean streams, as shown in Equation 3-2. Because freshwater is assumed to be pure, none of it can be sent to the regenerator network or effluent stream. It is also prohibited to send freshwater to the waste stream.

$$F^{FW} = \sum_{j=1}^{J} f^{FW}{}_j \qquad (3\text{-}2)$$

3.2.2 Material Balances for Outlet Streams

Lean streams can receive water from the freshwater stream, feed streams, the regenerator permeate or retentate streams and the pressurisation/depressurisation streams as shown in Equation 3-3. Since it is desirable to minimize the freshwater consumed, wastewater generated and the load imposed on the regenerator network, the wastewater sink is only used as a final resort and cannot receive water from the freshwater source or permeate streams. Only the original feed streams and the regenerator retentate streams can be sent to the wastewater stream as demonstrated in Equation 3-4. The concentration in sinks and the wastewater stream is dependent on the concentrations and flowrates of incoming streams, as shown in Equations 3-5 and 3-6, respectively.

$$f_j = f^{FW}{}_j + \sum_{i=1}^{I} f_{i,j} + \sum_{q=1}^{Q} f^P{}_{q,j} + \sum_{q=1}^{Q} f^R{}_{q,j} + \sum_{\mathrm{nt}=1}^{NT} f^{NT}{}_{nt,j} + \sum_{\mathrm{np}=1}^{NP} f^{NP}{}_{np,j} \qquad \forall j \in J \tag{3-3}$$

$$f^{WW} = \sum_{i=1}^{I} f^{WW}{}_i + \sum_{q=1}^{Q} f^{R,WW}{}_q + \sum_{\mathrm{nt}=1}^{NT} f_{nt}{}^{WW} + \sum_{\mathrm{np}=1}^{NP} f_{np}{}^{WW} \tag{3-4}$$

$$\begin{aligned} f_j c_{j,m} = \sum_{i=1}^{I} f_{i,j}\, C_{i,m} + \sum_{q=1}^{Q} f^P{}_{q,j} C^P{}_{q,m} \sum_{q=1}^{Q} f^R{}_{q,j} C^R{}_{q,m} \qquad & \forall j \in J; \\ & \forall m \\ + \sum_{\mathrm{nt}=1}^{NT} f^{NT}{}_{nt,j} C^{NT}{}_{nt,m} + \sum_{\mathrm{np}=1}^{NP} f^{NP}{}_{np,j} C^{NP}{}_{np,m} \end{aligned} \tag{3-5}$$

$$\begin{aligned} f^{WW} c^{WW}{}_m = \sum_{i=1}^{I} f_i^{WW} C_{i,m} + \sum_{q=1}^{Q} f^{R,WW}{}_q C^R{}_{q,m} \\ + \sum_{\mathrm{nt}=1}^{NT} f_{nt}{}^{WW} C^{NT}{}_{nt,m} + \sum_{\mathrm{np}=1}^{NP} f_{np}{}^{WW} C^{NP}{}_{np,m} \qquad \forall m \in M \end{aligned} \tag{3-6}$$

Because the freshwater stream is assumed to be pure, the contaminant balance in Equation 3-5 does not include a freshwater component. It is, however, not always possible or economical to obtain pure freshwater. If the freshwater used contains some amount of contaminant, this will have an effect on the freshwater requirement and must therefore be factored into the material balances. In such cases, Equation 3-5 needs to be modified as follows:

$$f_j c_{j,m} = f^{FW}{}_j C^{FW}{}_i \sum_{i=1}^{I} f_{i,j}\, C_{i,m} + \sum_{q=1}^{Q} f^{P}{}_{q,j} C^{P}{}_{q,m} \sum_{q=1}^{Q} f^{R}{}_{q,j} C^{R}{}_{q,m} + \sum_{\mathrm{nt}=1}^{NT} f^{NT}{}_{nt,j} C^{NT}{}_{nt,m} + \sum_{\mathrm{np}=1}^{NP} f^{NP}{}_{np,j} C^{NP}{}_{np,m} \qquad \forall j \in J;\ \forall m \qquad (3\text{-}5b)$$

Each sink has a maximum concentration limit, which is determined using the purity required for end-use in that sink. In the case of the wastewater sink, the limit is dictated by environmental restrictions. Constraints 3-7 and 3-8 ensure that these limits are observed.

$$C_{j,m}{}^{U} \geq c_{j,m} \qquad \forall j \in J; \forall m \in M \qquad (3\text{-}7)$$

$$C_m{}^{WW^U} \geq c_m{}^{WW} \qquad \forall m \in M \qquad (3\text{-}8)$$

3.2.3 Material Balances for Pumps and Turbines

The total flow through the PDISDB and PDMB via node *np* or *nt* is the sum of flowrates entering that node from the feed and regenerators, as shown in Equations 3-9 and 3-11. The corresponding concentration balances are shown in Equations 3-10 and 3-12.

$$f_{np} = \sum_{\mathrm{i}=1}^{I} f_{i,np} + \sum_{q=1}^{Q} f^{P}{}_{q,np} + \sum_{q=1}^{Q} f^{R}{}_{q,np} \qquad \forall np \in NP \qquad (3\text{-}9)$$

$$f_{np}c_{np,m} = \sum_{i=1}^{I} f_{i,np}C_{i,m} + \sum_{q=1}^{Q} f^{P}{}_{q,np}c^{P}{}_{q,m} + \sum_{q=1}^{Q} f^{R}{}_{q,np}c^{R}{}_{q,m} \qquad \forall np \in NP; \forall m \in M \tag{3-10}$$

$$f_{nt} = \sum_{i=1}^{I} f_{i,nt} + \sum_{q=1}^{Q} f^{P}{}_{q,nt} + \sum_{q=1}^{Q} f^{R}{}_{q,nt} \qquad \forall nt \in NT \tag{3-11}$$

$$f_{nt}c_{nt,m} = \sum_{i=1}^{I} f_{i,nt}C_{i,m} + \sum_{q=1}^{Q} f^{P}{}_{q,nt}c^{P}{}_{q,m} + \sum_{q=1}^{Q} f^{R}{}_{q,nt}c^{R}{}_{q,m} \qquad \forall nt \in NT; \forall m \in M \tag{3-12}$$

Flow going through these nodes after pressurisation or depressurisation can be distributed to any of the regenerator stages or sent directly to the sinks and wastewater stream.

$$f_{np} = \sum_{q=1}^{Q} f_{np,q} + \sum_{j=1}^{J} f_{np,j} + f_{np}{}^{WW} \qquad \forall np \in NP \tag{3-13}$$

$$f_{nt} = \sum_{q=1}^{Q} f_{nt,q} + \sum_{j=1}^{J} f_{nt,j} + f_{nt}{}^{WW} \qquad \forall nt \in NT \tag{3-14}$$

3.2.4 Material Balances for the Regenerator Network

The amount and concentration of feed to each stage $q \in Q$ of the regenerator network is dependent on the flow coming from the nodes to that stage, as shown in Equations 3-15 and 3-16

$$f^{F}{}_{q} = \sum_{np=1}^{NP} f_{np,q} + \sum_{nt=1}^{NT} f_{nt,q} + \sum_{i=1}^{I} f_{i,q} \qquad \forall q \in Q \tag{3-15}$$

$$f^{F}{}_{q}c^{F}{}_{q,m} = \sum_{\mathrm{np}=1}^{NP} f_{np,q}\ c_{np,m} + \sum_{\mathrm{nt}=1}^{NT} f_{nt,q}\ c_{nt,m} + \sum_{\mathrm{i}=1}^{I} f_{i,q}\ C_{i,m} \qquad \forall q\ \in Q;\ \forall m\ \in M \tag{3-16}$$

Equations 3-17 and 3-18 demonstrate that feed entering the regenerator is split into the permeate, a lean stream of low contaminant concentration, as well as the retentate, which contains a high contaminant concentration. The ratio of feed that reports in the permeate is known as the liquid recovery or liquid yield and is represented as Y_q in Equation 3-19. The permeate concentration is dependent on the removal ratio (RR_q), as shown in Equation 3-20. The removal ratio represents the amount of solute recovered in the retentate. In BB models, this value is a parameter, whereas detailed regenerator models use a variable recovery ratio.

$$f^{F}{}_{q} = f^{P}{}_{q} + f^{R}{}_{q} \qquad \forall q\ \in Q \tag{3-17}$$

$$f^{F}{}_{q}c^{F}{}_{q,m} = f^{P}{}_{q}c^{P}{}_{q,m} + f^{R}{}_{q}c^{R}{}_{q,m} \qquad \forall q\ \in Q;\ \forall m\ \in M \tag{3-18}$$

$$Y_q = \frac{f^{P}{}_{q}}{f^{F}{}_{q}} \qquad \forall q\ \in Q \tag{3-19}$$

$$c^{p}{}_{q,m} = (1 - rr_{q,m})c^{f}{}_{q,m} \qquad \forall q\ \in Q;\ \forall m\ \in M \tag{3-20}$$

Permeate and retentate streams leaving the regenerator stages can be sent to PDISDB for pressurisation/depressurisation before being recycled to the regenerator stages or discharged to the sinks. They can also be sent directly to the sinks, and retentate can additionally be sent directly to the waste stream. This is stated in Equation 3-21 for permeate and Equation 3-22 for the retentate.

$$f^{P}{}_{q} = \sum_{np=1}^{NP} f^{P}{}_{q,np} + \sum_{nt=1}^{NT} f^{P}{}_{q,nt} + \sum_{j=1}^{J} f^{P}{}_{q,j} \qquad \forall q \in Q \qquad (3\text{-}21)$$

$$f^{R}{}_{q} = \sum_{np=1}^{NP} f^{R}{}_{q,np} + \sum_{nt=1}^{NT} f^{R}{}_{q,nt} + \sum_{j=1}^{J} f^{R}{}_{q,j} + f^{R}{}_{q}{}^{WW} \qquad \forall q \in Q \qquad (3\text{-}22)$$

It must be ensured that the inlet feed to the regenerator is below the maximum allowable limit recommended by manufacturers. This is represented in constraint 3-23.

$$C^{U}{}_{q,m} \geq c^{F}{}_{q,m} \qquad \forall q \in Q;\ \forall m \in M \qquad (3\text{-}23)$$

3.3 Pressure Constraints

Pumps can only increase, while turbines can only decrease pressure. This is ensured by Equations 3-24 and 3-25.

$$p^{out}{}_{np} - p^{in}{}_{np} \geq 0 \qquad \forall np \in NP \qquad (3\text{-}24)$$

$$p^{in}{}_{nt} - p^{out}{}_{nt} \geq 0 \qquad \forall nt \in NT \qquad (3\text{-}25)$$

Streams must mix at equal pressures as dictated by constraints 3-26 to 3-37.

$$\left(p^{in}{}_{np} - P_{i}\right) f_{i,np} = 0 \qquad \forall i \in I\ ;\ \forall np \in NP \qquad (3\text{-}26)$$

$$\left(p^{in}{}_{nt} - P_i\right) f_{i,nt} = 0 \qquad \forall i \in I \text{ ; } \forall nt \in NT \quad (3\text{-}27)$$

$$\left(p^{in}{}_{np} - p^{P}{}_{q}\right) f^{P}{}_{q,np} = 0 \qquad \forall q \in Q \text{ ; } \forall np \in NP \quad (3\text{-}28)$$

$$\left(p^{in}{}_{np} - p^{P}{}_{q}\right) f^{R}{}_{q,np} = 0 \qquad \forall q \in Q \text{ ; } \forall np \in NP \quad (3\text{-}29)$$

$$\left(p^{in}{}_{nt} - p^{R}{}_{q}\right) f^{R}{}_{q,nt} = 0 \qquad \forall q \in Q \text{ ; } \forall nt \in NT \quad (3\text{-}30)$$

$$\left(p^{out}{}_{np} - p^{F}{}_{q}\right) f_{np,q} = 0 \qquad \forall q \in Q \text{ ; } \forall np \in NP \quad (3\text{-}31)$$

$$\left(p^{out}{}_{nt} - p^{F}{}_{q}\right) f_{nt,q} = 0 \qquad \forall q \in Q \text{ ; } \forall nt \in NT \quad (3\text{-}32)$$

$$\left(p^{out}{}_{np} - P_j\right) f_{np,j} = 0 \qquad \forall j \in J \text{ ; } \forall np \in NP \quad (3\text{-}33)$$

$$\left(p^{out}{}_{nt} - P_j\right) f_{nt,j} = 0 \qquad \forall j \in J \text{ ; } \forall nt \in NT \quad (2)$$

$$\left(p^{out}{}_{nt} - P^{WW}\right) f_{nt}{}^{WW} = 0 \qquad \forall nt \in NT \quad (3\text{-}35)$$

$$\left(p^{R}{}_{q} - P^{WW}\right) f^{R}{}_{q}{}^{WW} = 0 \qquad \forall q \in Q \quad (3\text{-}36)$$

$$\left(p^{P}{}_{q} - P_j\right) f^{P}{}_{q,j} = 0 \qquad \forall q \in Q \text{ ;} \forall j \in J \quad (3\text{-}37)$$

3.4 Regenerator Model

The permeate flux, jv_q, is characterized in terms of the membrane hydraulic permeability, the hydraulic pressure drop across the membrane and the solute rejection coefficient, as shown in Equation 3-38. The hydraulic permeability is the flux of water through the membrane per unit driving force. The driving force in nanofiltration is the transmembrane pressure difference.

$$jv_q = a_q(\Delta p_q - \Delta\pi_q) \qquad \forall q \in Q \tag{3-38}$$

Where

$$\Delta\pi_q = \mathrm{RT}\sum_{\mathrm{m}=1}^{M} \sigma_{q,m}({c^*}_{q,m} - {c^p}_{q,m}) \qquad \forall q \in Q \tag{3-39}$$

In the Spiegler-Kedem model, the removal ratio is calculated using the solute rejection coefficient and a dimensionless variable, $\kappa_{q,m}$, calculated using the reflection coefficient, water flux and solute permeability as shown in Equation 3-40. The solute rejection coefficient, $\sigma_{q,m}$, is defined as a measure of the fraction of the membrane through which the solute will not be transported (Vassilis, 1986). No rejection occurs when $\sigma_{q,m}$ is zero 0 and 100% rejection occurs when $\sigma_{q,m}$ is 1.

$$rr_{q,m} = \frac{\sigma_{q,m}(1 - \sigma_{q,m}\,\kappa_{q,m})}{1 - \sigma_{q,m}\,\kappa_{q,m}} \qquad \forall q \in Q;\ \forall m \in M \tag{3-40}$$

$$\kappa_{q,m} = \exp -jv_q\left(\frac{1 - \sigma_{q,m}}{\beta_{q,m}}\right) \qquad \forall q \in Q;\ \forall m \in M \tag{3-41}$$

The retentate pressure is calculated using the feed pressure and transmembrane pressure drop as shown in Equation 3-42. The permeate is assumed to be at atmospheric pressure. The number of modules per regenerator stage depends on the permeate flux and the required permeate flowrate. While it is desirable to minimize the number of modules in order to lower the capital costs of the membrane, this increases the feed pressure required for the same flowrate, thereby raising the operational cost due to energy. It is thus important to optimize this trade-off.

$$p^R{}_q = p^F{}_q - \Delta p_q \qquad \forall q \in Q \tag{3-42}$$

$$n_q = \frac{f^p{}_q}{jv_q\, s_q} \qquad \forall q \in Q \tag{3-43}$$

The effective area of a membrane module is calculated using its inner and outer diameters, $\emptyset_q{}^I$ and $\emptyset_q{}^O$, module length, l_q, and the packing density of the membrane within the module, η, as shown in Equation 3-44. Packing density is defined as the membrane active surface area per unit volume. A packing density of 800 m^2 m^{-3} was assumed.

$$s_q = 0.25\eta\, \pi \left(\emptyset_q{}^{O^2} - \emptyset_q{}^{I^2} \right) l_q \qquad \forall q \in Q \tag{3-44}$$

The cost of a module per unit area decreases as the size of the module increases. It was thus necessary to develop a correlation to represent this variation, thereby realistically representing the capital cost of the membrane. Equation 3-45 shows the correlation obtained by plotting the area of the three most common module sizes (2540, 4040 and 400) against their average price in US dollars.

$$K^{mem}{}_q = 19.754 s_q + 269 \qquad \forall q \in Q \tag{3-45}$$

The following equations from the Steric Hindrance Pore model are used to characterise the physical properties of the membrane. The pure water permeability of the membrane is calculated using the Hagen-Poiseuille equation (3-46), where ${}^{\Delta x}/_{\varepsilon_q}$ is the ratio of membrane thickness to its porosity, and μ is the viscosity of water.

$$a_q = \frac{{rp_q}^2}{8\,\mu\,{}^{\Delta x}/_{\varepsilon_q}} \qquad \forall q \in Q \tag{3-46}$$

The steric factors for the diffusion, $k^D{}_{q,m}$, and convection, $k^C{}_{q,m}$, of each solute are calculated using $\lambda_{q,m}$, the ratio of the solute radius to pore radius.

$$\lambda_{q,m} = \frac{rs_m}{rp_q} \qquad \forall q \in Q; \forall m \in M \tag{3-47}$$

$$k^D{}_{q,m} = (1 - \lambda_{q,m})^2 \qquad \forall q \in Q; \forall m \in M \tag{3-48}$$

$$k^C{}_{q,m} = 2(1 - \lambda_{q,m})^2 - (1 - \lambda_{q,m})^4 \qquad \forall q \in Q; \forall m \in M \tag{3-49}$$

The solute permeability, $\beta_{q,m}$, is calculated using the solute's diffusivity, D_m, the steric factor for diffusion, $k^D{}_q$, and ${}^{\Delta x}/_{\varepsilon_q}$.

$$\beta_{q,m} = \frac{D_m\, k^D{}_{q,m}}{{}^{\Delta x}/_{\varepsilon_q}} \qquad \forall q \in Q; \forall m \in M \tag{3-50}$$

The reflection coefficient, $\sigma_{q,m}$, is calculated using Equation 3-51. $\sigma_{q,m}$ can only be a positive value between 0 and 1. To satisfy this condition, where $\lambda_{q,m}$ is greater than 1, $\sigma_{q,m}$ should automatically become 1. This is because a $\lambda_{q,m}$ that is greater than 1 implies that it is not physically possible for the solute to pass through the pores of the membrane, therefore a theoretical rejection of 100% is obtained, corresponding to a reflection coefficient of 1. In this model, a binary variable, $z_{q,m}$, is introduced to enforce this condition as shown in Equations 3-51(b) and 3-51(c). Where $\lambda_{q,m}$ is greater than 1, $z_{q,m}$ becomes 0 and $\sigma_{q,m}$ becomes 1. For values of $\lambda_{q,m}$ that are less than 1, $z_{q,m}$ becomes 1 and $\sigma_{q,m}$ is calculated accordingly.

$$\sigma_{q,m} = 1 - k^{C}{}_{q,m}\left(1 + \frac{16}{9}\lambda_{q,m}{}^{2}\right) \qquad \forall q \in Q; \forall m \in M \tag{3-51}$$

$$\sigma_{q,m} = 1 - z_{q,m}\left(k^{C}{}_{q,m}\left(1 + \frac{16}{9}\lambda_{q,m}{}^{2}\right)\right) \qquad \forall q \in Q; \forall m \in M \tag{3-51(b)}$$

$$z_{q,m} > 1 - \lambda_{q,m} \qquad \forall q \in Q; \forall m \in M \tag{3-51(c)}$$

3.5 Costing

A cost estimate is included in the model, incorporating the annualised capital and operating costs associated with regeneration, as well as the cost of wastewater discharge. The capital cost is inclusive of the cost of the membrane system and housing, the cost of pumps and turbines as well as installation costs. The operating and maintenance costs are inclusive of cleaning and anti-fouling chemicals, repair, maintenance and replacement costs, labour costs and power costs. The financial benefit obtained from energy recovery is also accounted for in the cost estimate.

3.5.1 *Annualised Capital Cost*

The annualised capital cost, represented in Equation 3-52, incorporates the annualised cost of membrane modules, pumps, turbines, as well as the installation cost, which is a function of the cost of membrane modules.

$$\begin{aligned} ac^{CAP} = & \sum_{q=1}^{Q} \frac{n_q Cost_q^{mem}}{LT^{mem}} + \sum_{np=1}^{NP} Cost^{pu}(f_{np}(p_{np}^{out} - p_{np}^{in}))^{0.79} \\ & + \sum_{nt=1}^{NT} Cost^{tu}(f_{nt}(p_{nt}^{in} - p_{nt}^{out}))^{0.47} \\ & + Cost^{inst}\left(\frac{LT^{mem}}{LT^{inst}}\right) \sum_{q=1}^{Q} \frac{n_q Cost_q^{mem}}{LT^{mem}} \end{aligned} \tag{3-52}$$

3.5.2 *Annualised Operational Cost*

The labour cost, cleaning and chemical costs, electrical costs for the pumps and turbines, membrane operational costs and plant maintenance costs are incorporated in the annualized operational cost as shown in Equation 3-53.

$$\begin{aligned} ac^{OP} = \mathbf{AOT}\Bigg(& \sum_{q=1}^{Q} f_q^F (Cost^{clean} + Cost^{chem}) + Cost^{lab} time^{lab} + \\ & \sum_{np=1}^{NP} \frac{Cost^{elec}}{3600}\left(\frac{f_{np}(p_{np}^{out} - p_{np}^{in}))}{\eta}\right) - \sum_{nt=1}^{NT} \frac{Cost^{elec}}{3600}\left(\frac{f_{nt}(p_{nt}^{in} - p_{nt}^{out})}{\eta}\right)\Bigg) + ac^{CAP} Cost^{main} \end{aligned} \tag{3-53}$$

3.5.3 *Annual Water Cost*

The water cost consists of the cost of freshwater as well as the cost of wastewater disposal.

$$ac^{W} = AOT(f^{WW}Cost^{WW} + f^{FW}Cost^{FW}) \qquad (3\text{-}54)$$

3.5.4 Objective Function

The objective function is to minimise the total annualised cost (TAC) of the network, comprising the annualised capital cost, annualised operation costs and annual water cost.

$$\min \{ac^{CAP} + ac^{OP} + ac^{W}\} \qquad (3\text{-}55)$$

This objective function was formulated to obtain a result that provides the most optimal environmental benefit without compromising the profits of the operation, but rather enhancing them by reducing the water cost. This 'win-win' approach makes the proposed framework lucrative and easily adoptable because businesses exist to make a profit, and decision-makers tend to only focus on their 'bottom line'. There has, however, been a thrust for industries to consider other aspects in addition to the economics, and sometimes adopt strategies that promote such aspects, even when the changes are not economically optimal. In cases where the economics of the operation can be compromised in favour of other competing objectives, the framework can be reformulated into a multi-objective optimization problem by assessing the relative importance of each competing objective and thereafter assigning weighting factors to each objective.

References

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Jeżowski, Jacek. 2010. “Review of Water Network Design Methods with Literature Annotations.” *Industrial & Engineering Chemistry Research* 49 (10): 4475–4516. https://doi.org/10.1021/ie901632w.

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Nomenclature

Sets

I	sources
J	Water using streams
M	solutes
NP	Pumping nodes
NT	Turbine nodes
Q	Regenerator stages

Parameters

A_q	Pure water permeability **(m h^{-1} bar $^{-1}$)**
AOT	Annual Operating Time **(h)**
C	Concentration **(mol m^{-3})**

$Cost$	Costing parameter **($)**
F	Flowrate **(m^3 h^{-1})**
P	Pressure **(bar)**
R	Ideal gas constant **(m^3 bar K^{-1} mol^{-1})**
T	Temperature **(K)**
α	Liquid recovery
η	Packing density of module **(m^{-1})**

Variables

ac	Annual Cost **($ y^{-1})**
a	Pure water permeability **(m h^{-1} bar^{-1})**
b	Solute permeability **(m h^{-1})**
c	Concentration **(mol m^{-3})**
f	Flowrate **(m^3 h^{-1})**
jv	Permeate flux **(m h^{-1})**
k^D	Steric factor for diffusion

k^C	Steric factor for convection
l	Length of module **(m)**
nm	Number of modules
p	Pressure **(bar)**
rr	Removal ratio
s	Area per module **(m^2)**
x	Binary variable for existence
$\Delta\pi$	Osmotic pressure drop **(bar)**
σ	Rejection coefficient
κ	Dimensionless variable
β	Solute permeability
η	Packing density of module
$\varnothing^I$	Inner diameter of module **(m)**
$\varnothing^I$	Outer diameter of module **(m)**

λ	Ratio of solute radius to pore radius
$\Delta x/_{\varepsilon}$	Ratio of membrane's thickness to its porosity
μ	Viscosity of water **(x10^{-9} bar h)**
z	Binary selection variable

Superscripts

CAP	Capital
$chem$	Chemicals
$clean$	Cleaning
F	Feed
FW	Freshwater
in	Inlet of pressure node
$inst$	installation
L	Lower Bound
mem	membrane
out	Exit of pressure node

P	Permeate
pu	pumps
R	Retentate
tu	turbines
U	Upper bound
WW	Wastewater

Chapter 4

Results and discussion

In this chapter, the applicability of the model is demonstrated using an illustrative example adapted from literature.

4.1 Illustrative example

The example used in this chapter is adapted from Chew et al. (Chew et al. 2008). The water network, shown in Figure 4-1, is comprised of an integrated pulp mill and bleached paper plant, containing four sources and four sinks.

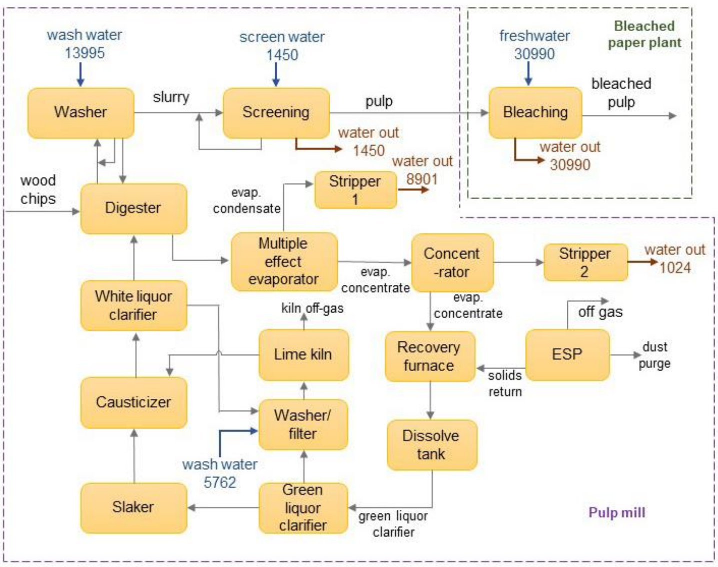

Figure 4-1: Process flow diagram for illustrated example

Data for the sinks and sources are shown in Table 4-1. The contaminants present are chlorine (Cl^-), magnesium (Mg^{2+}) and sodium (Na^+) ions. Their diffusivities and Stokes' radii are shown in Table 4-2 (Hussain, Abashar, and Al-Mutaz 2006). While this example includes three contaminants, the fixed flowrate approach used in the formulation allows the developed framework to be adapted to accommodate any number and type of contaminants in any sector of industry. This flexibility also means that contaminants can be added or removed at any stage of the design process and recalculations made as new information becomes available. This only entails modifying the set of contaminants, introducing the parameters applicable to additional contaminants, and recalculating the result. In addition, the model can be scaled up or down to any size of plant. This would only require changing some parameters such as stream flowrates and costing factors. The embedded custom NF module design feature utilises ranges that incorporate most commercially available modules, from those normally used in pilot plants, to those normally used in large scale facilities.

Table 4-1: Data for sources and sinks

Sources, $i \in I$					**Sinks, $j \in J$**				
i	**Flowrate ($m^3\ h^{-1}$)**	**Concentration (mol m^{-3})**			***j***	**Flowrate ($m^3\ h^{-1}$)**	**Max. concentration (mol m^{-3})**		
		Cl^-	**Na^+**	**Mg^{2+}**			**Cl^-**	**Na^+**	**Mg^{2+}**
1	8901	0	0	0	1	13995	0.97	0.32	3.89
2	1450	8.7	36.6	2.96	2	1450	6.80	0.06	10.48
3	1024	0	0	0	3	5762	0	0	0
4	30950	14.1	21.75	0.13	4	30920	0.10	0.03	0.16
FW	variable	0	0	0	WW	variable	20	20	20

Table 4-2: Solute properties for illustrative example

	Cl^-	Na^+	Mg^{2+}
Bulk Diffusivity, D_m (x 10^{-9} m^2h^{-1})	7308	478	2593
Stokes' radius, rs_m (nm)	0.121	0.348	0.184
Reflection factor for NF90 membrane	0.594	0.677	0.731
Permeate solubility for NF90 membrane ($m\ h^{-1}$)	5.86 x 10^{-3}	2.77x10^{-6}	1.94x10^{-4}

In the absence of a regenerator network, the water network requires 39 832 $m^3\,h^{-1}$ of freshwater and discharges 30 000 $m^3\,h^{-1}$ of wastewater. Figure 4-2 shows the water network when there is water integration but no regeneration. The corresponding flowsheet is shown in Figure 4-3

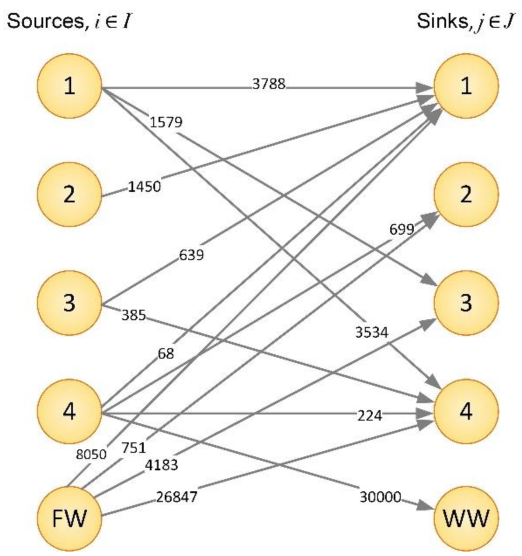

Figure 4-2: Optimal network for scenario A (no regenerator)

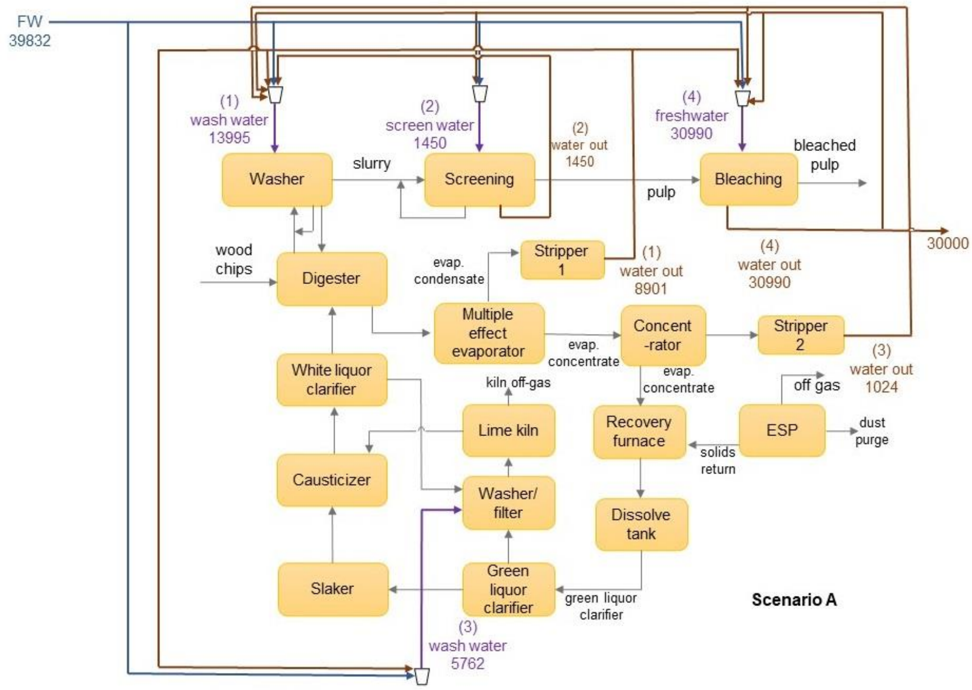

Figure 4-3: Optimal flowsheet for scenario A (no regenerator)

The optimisation was performed in GAMS version 34.3.0 using version 21.1.13 of the Branch and Reduce Optimisation Navigator (BARON). This solver uses a branch-and-reduce algorithm to find the global optimum in convex and nonconvex MINLPs (Tawarmalani and Sahinidis 2005). The criteria for convergence were an absolute gap (optcA) of 1 x 10^{-9} and relative optimality (optcR) of 0.1. Where convergence was not reached in 72 hours, the best results obtained by that time were reported. Four scenarios were investigated:

- Scenario A: a base case containing no regenerator.
- Scenario B: variable-stage regenerator assuming fixed removal ratio (black-box approach).
- Scenario C: variable stage regenerator network containing up to four stages of modules with fixed properties, having a variable removal ratio based on the Spiegler-Kedem model.

- Scenario D: variable stage regenerator network containing up to four stages of modules, having a variable removal ratio based on the Spiegler-Kedem model and variable module properties determined using the Steric Hindrance Pore model.

The following assumptions were made:

i. The plant operates for 8 000 hours per year.
ii. Isothermal operation at 298 K.
iii. The background process effluent and feed streams, as well as the regenerator network permeate streams are at atmospheric pressure.
iv. Fluid is Newtonian and the flow is steady, fully developed, incompressible and laminar, with a constant velocity of 1 m s^3, a viscosity of 0.89 cP and density of 1 kg m^{-3}.
v. Freshwater has negligible contaminant concentration.
vi. Regenerator stages have a liquid recovery of 70%.
vii. Pumps and turbines have an efficiency of 70%.

The costing parameters used are shown in Table 4-3. In scenarios B and C, the Dow FilmTec NF-90 module was assumed. Its properties were obtained from the manufacturer’s specification sheet (Dow Chemicals, n.d.) and literature sources (Nair et al. 2018; Al-Zoubi and Omar 2009). These are shown in Table 4-4. In scenario D, the ranges used as the lower and upper bounds for the properties of the customised modules were obtained from the datasheets of 76 modules, commercially available from several manufacturers, namely AMS Technologies, DeltaPore, Dow FilmTec ESNA Hydranautics, General Electric, Global Industrial Water, Koch Membrane Systems, Microdyn, Nair, Pentair and Synder. These values are shown in Table 4-5.

Table 4-3: Costing Parameters

Parameter	Symbol	Value
Cleaning cost ($ m^{-3})	$Cost^{clean}$	0.003
Chemical cost ($ m-3)	$Cost^{chem}$	0.01
Electrical cost ($ kW^{-1} h^{-1})	$Cost^{elec}$	0.15
Installation cost ($)	$Cost^{inst}$	0.333
Labour cost ($ h^{-1})	$Cost^{lab}$	12
Maintenance cost factor	$Cost^{main}$	0.05
Pumping cost parameter ($)	$Cost^{pu}$	0.016
Turbine cost parameter ($)	$Cost^{tu}$	0.418
Freshwater cost ($ m^{-3})	$Cost^{FW}$	1.30
Wastewater cost ($ m^{-3})	$Cost^{WW}$	2.20
Installation lifetime (y)	LT^{inst}	15
Membrane lifetime (y)	LT^{mem}	3
Hours of labour per week (h wk^{-1})	h^{lab}	20

Table 4-4: NF-90 module properties

Parameter	Symbol	Value
Area (m^2)	S_q	37
Pure water permeability (m h^{-1} bar^{-1})	a_q	0.0113
Pressure drop (bar)	Δp_q	<1.5
Operating pressure (bar)	${p^F}_q$	<40
Operating Flux (m h^{-1})	jv_q	< 0.03

Table 4-5: Ranges of module properties

Property	Symbol	Value
Inner diameter (in.)	${d_q}^i$	0.75 – 1.14
Outer diameter (in.)	${d_q}^O$	1.8 - 8

Length (m)	L_q	1 – 1.6
Area (m^2)	S_q	2.59 - 37
Pressure drop (bar)	Δp_q	<1.5
Operating pressure (bar)	$p^F{}_q$	<40
Operating Flux (m s^{-1})	jv_q	<13.9 ×10^{-5}

4.2 Results and discussion

Table 4-6 contains the solution statistics for the four scenarios. It can be noted that the introduction of a regeneration network greatly increases the number of variables and nonlinearity of the problem, which are exacerbated as the level of detail increases. The BARON solver uses the branch and reduce method to narrow down the search space and solve the problem (Tawarmalani and Sahinidis 2005). Due to the great nonlinearity of the detailed model, it was necessary to provide feasible initial points. The initial points were generated by taking the solution of the previous scenario and assigning corresponding initial values to the newly added variables (e.g. using the solution of scenario B to generate the starting point of scenario C). Furthermore, it was necessary to provide upper and lower bounds for all variables. Reformulation by substitution of intermediary values was used to decompose equations containing multiple nonlinear terms. An example is Equation (12), which was reformulated into Equations 12(a), 12(b) and 12(c).

$$\boldsymbol{\kappa_{q,m} = \exp -jv_q \left(\frac{1-\sigma_{q,m}}{\beta_{q,m}}\right)} \qquad \forall \boldsymbol{q} \in \boldsymbol{Q};\ \forall \boldsymbol{m} \in \boldsymbol{M} \ \textbf{(12)}$$

$$\boldsymbol{\kappa_{q,m}} = \mathbf{exp}(\chi_{q,m}) \qquad \forall \boldsymbol{q} \in \boldsymbol{Q};\ \forall \boldsymbol{m} \in \boldsymbol{M} \ \mathbf{(12(a))}$$

$$\chi_{q,m} = \boldsymbol{j v_q \zeta_{q,m}} \qquad \forall \boldsymbol{q} \in \boldsymbol{Q};\ \forall \boldsymbol{m} \in \boldsymbol{M} \ \mathbf{(12(b))}$$

$$\boldsymbol{\zeta_{q,m} \beta_{q,m} = 1 - \sigma_{q,m}} \qquad \forall \boldsymbol{q} \in \boldsymbol{Q};\ \forall \boldsymbol{m} \in \boldsymbol{M} \ \mathbf{(12(c))}$$

Table 4-6: Model statistics

Scenario	**A**	**B**	**C**	**D**
Single equations	43	1308	1332	1407
Single variables	44	1297	1325	1420
Nonlinear non-zero elements	6	2318	2386	2666
CPU time (s)	2.06	259200	259200	259200
OptcR	3.9 x10-9	0.32	0.38	0.37

The results obtained from the optimisation are shown in Table 4-7. In all scenarios, it was found that incorporating a regenerator network provided significant opportunities for cost reduction and environmental benefits. The BB model predicted higher freshwater and cost savings when compared to the detailed model using the same regenerator model. This was an expected result since the BB approach assumes a fixed removal ratio despite fluctuations in operational conditions such as the feed concentrations, inlet pressure and permeate flux. In reality, these conditions affect the removal ratio. Consequently, the omission of such key relationships makes it possible for the BB approach to consider some intrinsic constraints, which would otherwise be accounted for in more detailed models such as the Spiegler-Kedem. This allows the BB model to predict better performance at a lower cost when using the same parameters. The accuracy of any BB model is thus heavily reliant on the quality of the assumptions made. Similar conclusions have been made in systems containing reverse osmosis and electrodialysis regenerators (Nezungai 2016a; Abass and Majozi 2016a). When a design based on incorrect assumptions is implemented, this can give rise to problems such as performance issues, unnecessarily high capital or operational expenditure and capacity constraints. The use of detailed regeneration models enables a more realistic design process, thereby reducing the risk of over-designing or under-designing. The BB approach is thus ideal as a preliminary step but must be substituted with more detailed models as the design process progresses.

Table 4-7: Results Obtained for Illustrative Example

Scenario	**A**	**B**	**C**	**D**
Freshwater flowrate (m^3 h^{-1})	39832	33004	34000	23435
Wastewater flowrate (m^3 h^{-1})	30000	23172	24168	13603
Freshwater Savings	-	17.1%	15%	41%
TAC (M$ y^{-1})	94.2	89.2	90.9	58.4
Freshwater cost (M$ y^{-1})	51.8	34.3	35.4	24.4
Wastewater cost (M$ y^{-1})	42.4	40.8	42.5	23.9
Regeneration Cost (M$ y^{-1})	-	14.1	13.0	10.1
Cost Savings	-	5%	4%	38%
Optimal stages	-	2	2	1
CPU time (s)	1.16	259 200	259 200	259 200
OptcR	3.9×10^{-9}	0.32	0.38	0.37

Scenario D resulted in the highest cost and water savings when compared to the other scenarios. Figure 4-4 shows the results obtained for Scenario B, and Figure 4-5 shows the corresponding flowsheet. The optimal network and flowsheets for scenario C are shown in Figures 4-5 and 4-7 respectively, whereas those for scenario D are shown in Figures 4-8 and 4-9. It was found that the use of customised membrane modules can generate savings of up to 41% on the water consumption and 38% on the total annualised cost of the network. Two major factors that influenced the improvement are the improved removal ratio, as well as the reduction in the number of modules required.

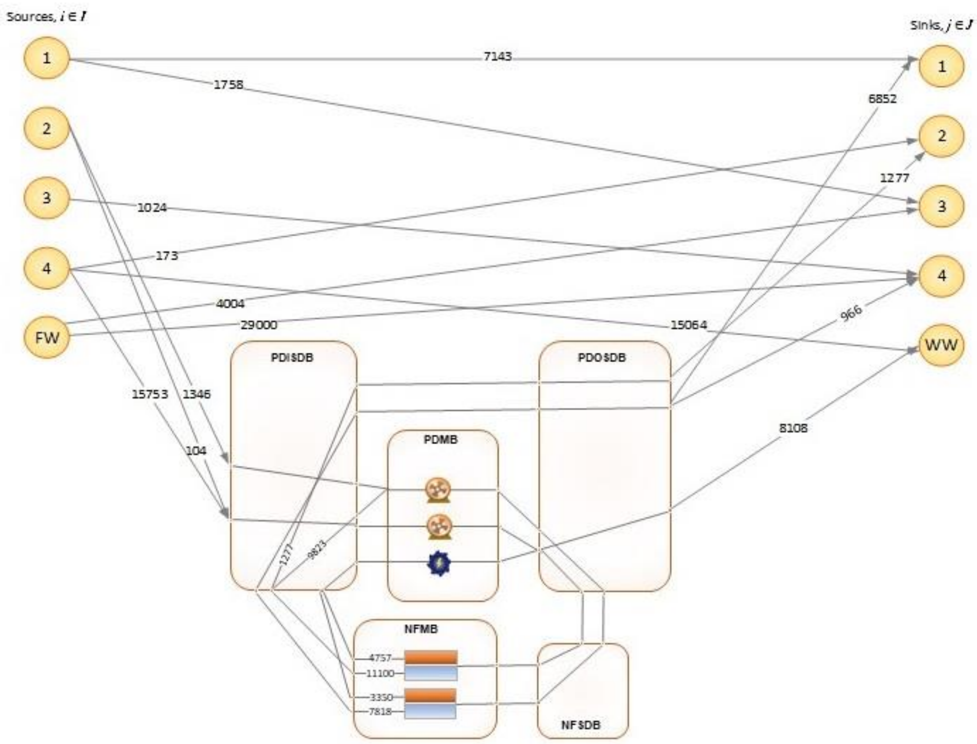

Figure 4-4:Optimal network for scenario B (black-box regenerator)

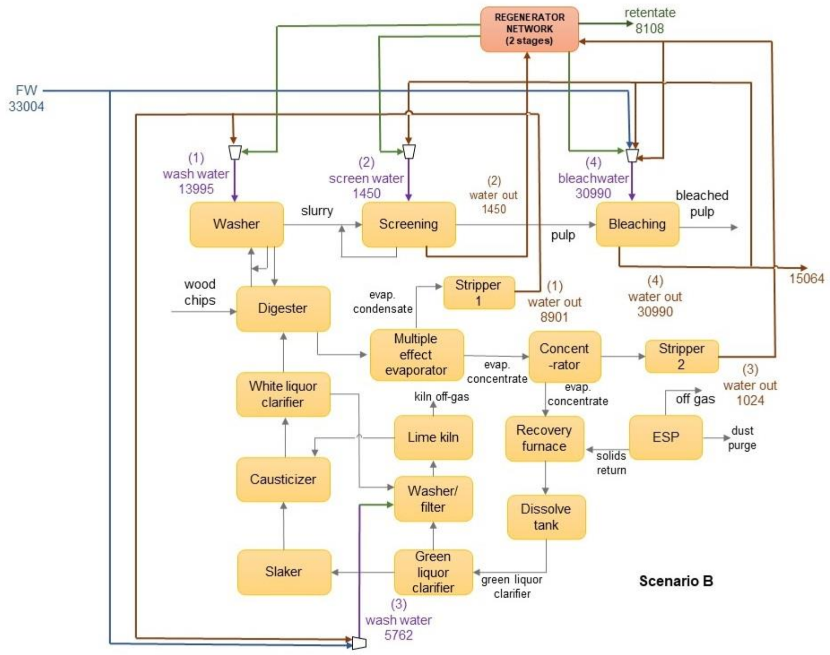

Figure 4-5: Optimal flowsheet for scenario B (black-box regenerator)

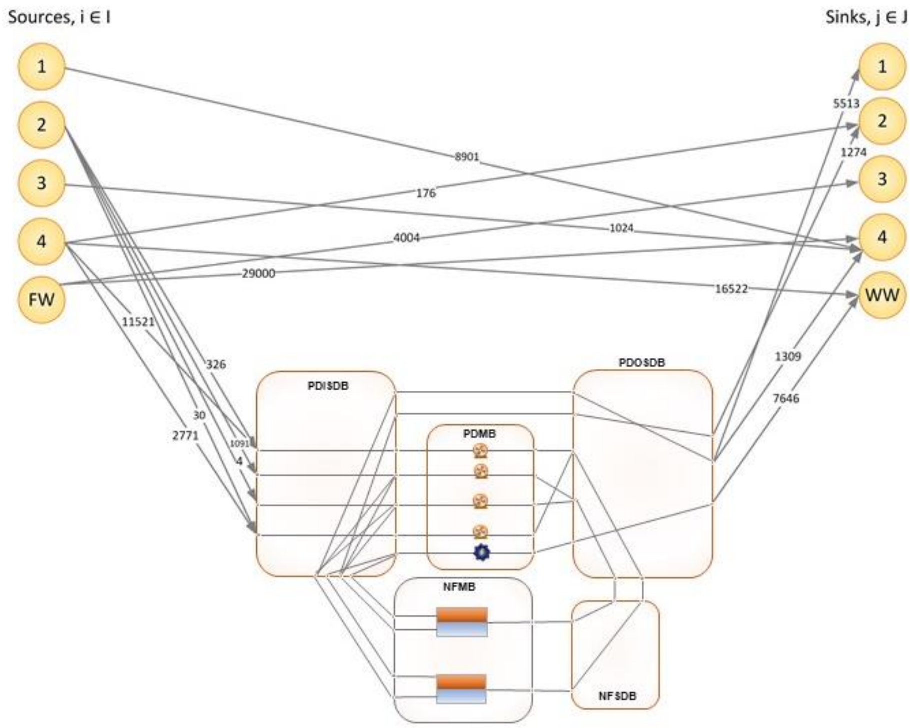

Figure 4-6: Optional network for scenario C (detailed regenerator model using predetermined modules)

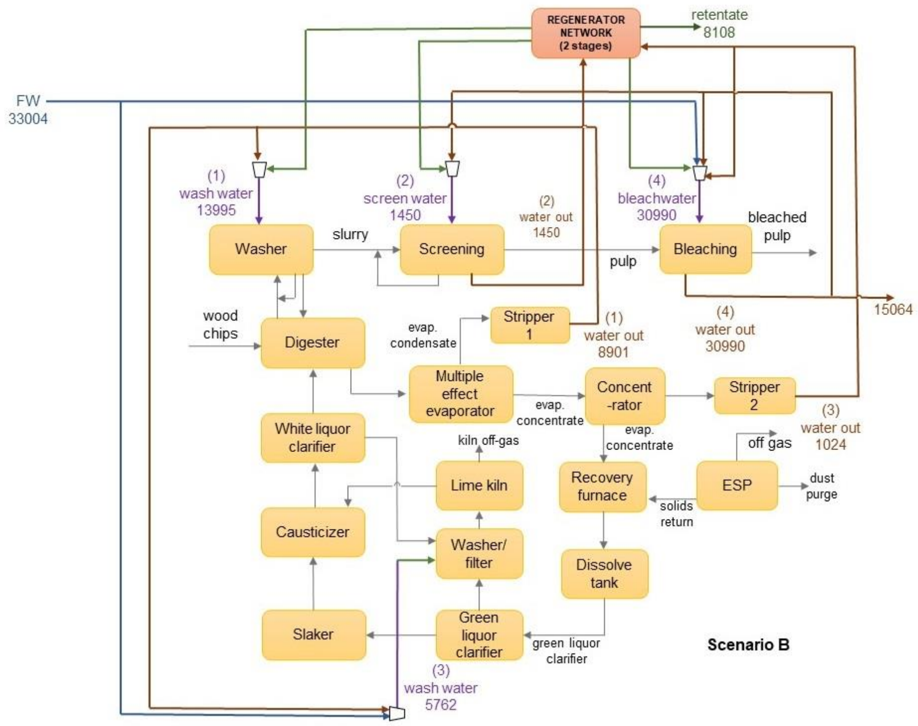

Figure 4-7: Optional flowsheet for scenario C (detailed regenerator model using predetermined modules)

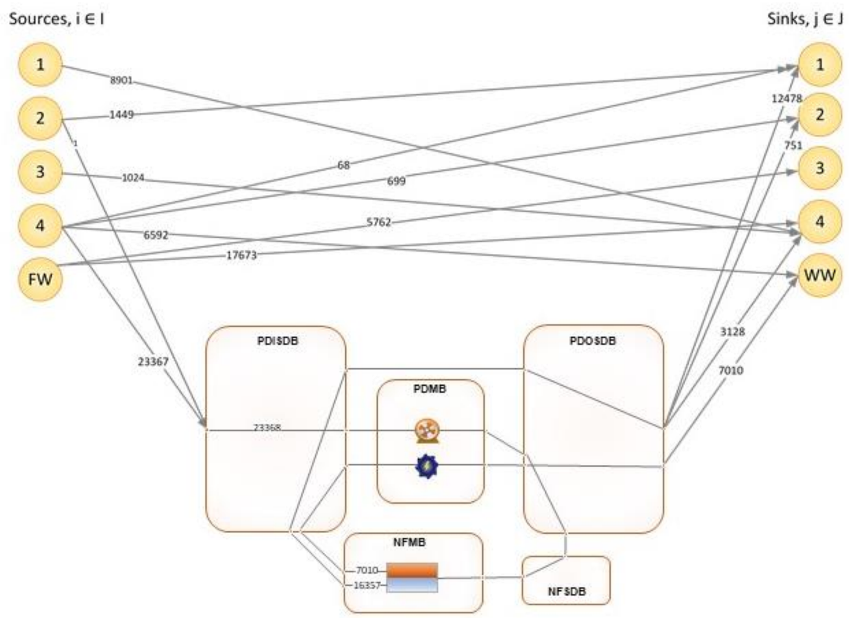

Figure 4-8: Optimal network for scenario D (detailed regenerator model with customised modules)

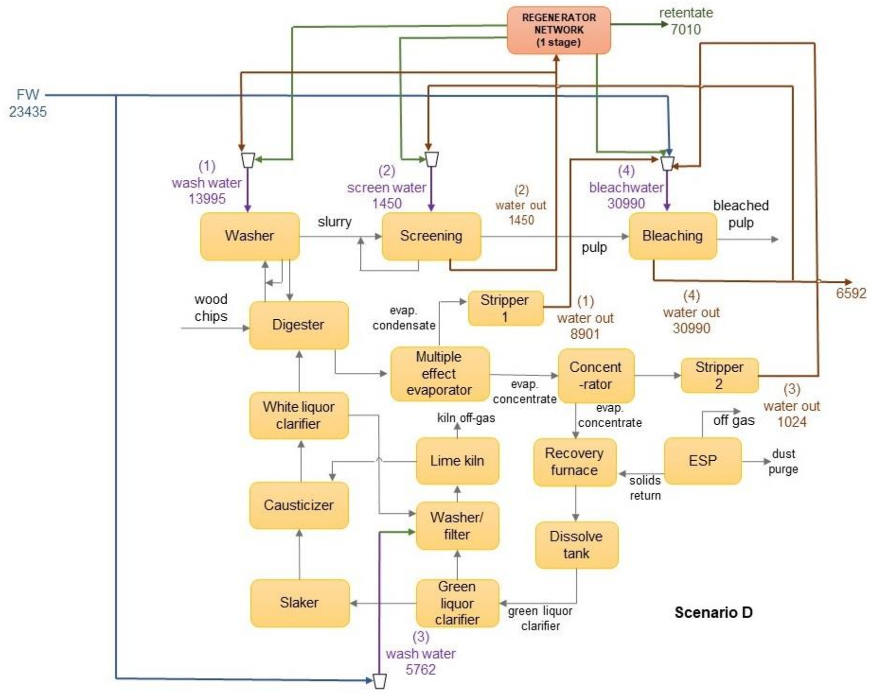

Figure 4-9: Optimal flowsheet for scenario D (detailed regenerator with customised modules)

A high removal ratio increases the quantity and quality of water that is available for reuse and recycle. This has a dual effect on the objective as it increases the number of sinks that can accept undiluted water from the permeate streams, whilst also increasing the permeate stream potency to dilute water from the sources, which would otherwise have been discarded as wastewater. Source 4 is the highest contributor to the wastewater flowrate in this study. Where there is no regenerator, 30 000 m^3 of water is sent from source 4 to the wastewater stream. In scenario C, the volume discarded is reduced to 16 522 m^3, with 14 292 m^3 being sent to the regenerator network. In scenario D however, only 6 592 m^3 is discarded, and 23 367 m^3 treated in the regenerator network. The product is used to dilute water from sources 2 and 3, allowing them to be fully utilised by the sinks without having to pass through the regenerator.

The bleaching section of a pulp and paper plant is a very sensitive area, and in some cases, water coming out of the departments before bleaching is expressly prohibited from being sent to the bleaching section. In this example, a minuscule amount of each component was allowed into this stream to facilitate the optimal usage of water, while not compromising the quality of the bleaching operation. As a result, most of the water used in the bleaching section was obtained from the freshwater stream in all four scenarios, as high dilution was required to achieve the maximum allowable contaminant concentration. There was, however, a significant reduction in the amount of freshwater directed to this stream after the incorporation of a customized regeneration network since it predicted a permeate of over 99% purity. In scenario A (no regeneration), 86% of water sent to bleaching was freshwater, whereas, in scenario D (containing a customized regeneration network), this amount was significantly reduced to 57%.

17 080 and 10 731 modules were required in scenarios B and C respectively, whereas scenario D only required 1 048 modules. Scenarios B and C required 2 regenerator stages and had a permeate recycle, therefore more regenerator modules were needed. Permeate recycles and multiple stages are useful when the desired concentration cannot be achieved in a single pass. Permeate recycles reduce the regenerator inlet concentration, thereby reducing concentration polarization. This results in an improvement in the overall removal ratio and product quality. The drawback of permeate recycles or systems containing permeate recycles and multiple stages in series is that they reduce the volume productivity of the regenerator.

Another factor that affects the number of modules is the permeate flux, which is directly proportional to permeate flowrate. This means that operating at a higher flux also reduces the number of modules required. This however normally comes at an energy expense, as more pressure is required to increase the permeate flux. Scenario B had an energy cost of $6.3 million, whereas that of scenario D was $7.2 million.

The number of modules has a significant effect on the annualised capital cost. There is, however a trade-off between the capital costs and operational costs. Whilst lower capital costs also imply lower labour, maintenance and cleaning costs, energy costs form the bulk of the operational costs in a regeneration facility. More energy is required to obtain the increased fluxes and higher removal ratios which enable better performance with lower capital investment. For example, Scenario B, whose capital cost was $6.1 million, and an operational cost of $8.1 million, with an energy cost of $4.9 million. On the other hand, scenario D, whose capital cost was only $0.4 million, had a higher operational cost of $9.6 million, with an energy cost of $7.2 million. Furthermore, energy costs only account for 5% of the TAC in scenario B, but they account for 12% of the cost of scenario D. From the results obtained, it can be observed that the trade-off between energy costs, capital costs and water savings is complex. This complexity is further exacerbated by the fact that energy is also currently a finite and scarce resource.

The properties of the module designed by the model in scenario D are shown in Table 4-8. The membrane has a pore radius of 0.121 nm. This radius allows a removal ratio of 100% to be theoretically achieved for all three contaminants in this system, as the ratio of solute radius to pore radius will be greater than one. Geometrically, the modules have an inner diameter of 0.019 inches, an outer diameter of 0.203 inches, a length of 1.216 m and an area of 31.3 m^2. This is comparable to most 'large size' modules that are available in the market. There is a negative correlation between the module sizes and their cost per unit area. It is thus usually prudent to buy larger modules, especially for processes that have a high throughput. Based on a comparison between scenarios C and D, it is apparent that the choice of module has a significant impact on the effectiveness of the regenerator network in reducing costs and making the process more environmentally sustainable. The quality of water from sources, requirements in the sinks, and the nature of contaminants present are key factors when assessing the suitability of a membrane for treating water in a process. There are heuristics available for selecting modules, and salespeople and manufacturers are well versed with the limitations of the various available membranes, as well as the types of water that best suit them. There is, however, room for error in this type of qualitative analysis. The use of models such as the one developed in this study is useful in sense-checking qualitative decisions and providing ideas and opportunities for the development of innovative, process-specific solutions. In a case where multiple regenerator stages are present, the model can predict whether it is beneficial to have the same type and size of module in all stages, or if it would be better to vary the stages as the feed concentrations also vary.

Table 4-8: Module properties for customised module

Module property	Value
Inner diameter (in.)	0.019

Outer diameter (in.)	0.203
Length (m)	1.216
Module area (m^2)	31.3
Pressure drop (bar)	1.29
Operating Flux (ms^{-1})	5×10^{-5}

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Chapter 5

Conclusion & Future Work

This work addresses the optimal synthesis of multi-stage, multicontaminant nanofiltration regenerator networks for application in water minimisation. The resultant MINLP formulation was applied to an illustrative example and solved using the BARON solver. It was found that optimally designed regenerator networks have the potential to reduce the environmental impact of a chemical process, whilst also providing significant economic benefits. The study found that it is important to ensure that the model used for regeneration is as representative of the actual process as possible, as this significantly affects the accuracy of equipment sizing and cost estimates.

In future, it is recommended to explore methods and solvers that will enable the model to solve to optimality within a reasonable timeframe, despite the high level of detail. The research can also be expanded to incorporate multiple types of regenerators. The level of detail can also be further improved by using a more rigorous transport model such as the Donnan steric pore model (DSPM). Multi-objective optimisation can also be explored to incorporate abstract concepts and relationships.

The assumption of isothermal operation allowed the model to focus solely on the material balances, negating the need to incorporate the energy balance. It was necessary to limit the scope of this work to an isothermal operation due to the complexity of the nanofiltration model, which was the focus of this investigation. Whilst the model can be applied to non-isothermal operations as it is, great benefit can be derived from expanding the model to cater for temperature variations, and therefore simultaneously optimise the water and energy requirements. This is aligned to current trends in the field of water network synthesis and optimisation, fuelled by prevalent concerns around the water-energy nexus.

The operating cost factor used in the model proposed in this dissertation is inclusive of cleaning and anti-fouling chemicals, as well as maintenance and replacement costs. The model however assumes that the system will run at 100% capacity for the lifetime of the membranes. Whilst this was sufficient for the scope of the current research, it would be prudent to consider the effects of fouling on the capacity of the membrane. Fouling is a major concern in membrane-based water treatment systems, and remains a major obstacle to their adoption in industry (Shim et al., 2021). Incorporation of fouling would improve the accuracy and applicability of the model, whilst possibly providing insight into possible anti-fouling solutions. Fouling is an intricate phenomenon, and the study therof often results in complex mathemamatical models. Some factors that are known to influence membrane fouling include the membrane material, transmembrane pressure difference, operating parameters and the properties of the foulant. Various mechanistic models have been proposed based on some or all of these factors, however, their mathematical complexity has been a drawback in their widespread application.

More recently, artificial intelligence aproaches have been proposed as alternatives (Niu et al., 2022).

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