A PROCESS INTEGRATION TECHNIQUE FOR INTEGRATED WATER AND REGENERATION NETWORKS THAT ARE CHARACTERIZED BY VARIABLE REMOVAL RATIOS

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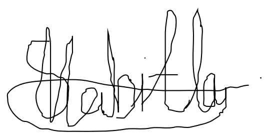
Declaration

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.



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Synopsis

Water management has become a very critical issue for process and manufacturing industries due to the escalating costs of freshwater and wastewater treatment. These costs arise from the rapid depletion of this natural resource and this has heightened the need for sustainable engineering within industry. The aim is to ensure that operations adhere to the stringent environmental regulations placed on wastewater discharge while optimizing on production. As a result, process integration is applied in industries for sustainable water management through exploiting opportunities of water reuse, recycle and regeneration. This can be achieved through optimization of the water network, which integrates the different water sources, sinks and regeneration units. However, upon the incorporation of a regenerator in the water network, the synthesis problem becomes very complex. As a result, water pinch analysis is integrated with mathematical modelling in this dissertation to help reduce both model complexity and convergence issues. To be attained from such a framework are conceptual insights of the water network from pinch analysis and rigorous designs from mathematical optimization. In literature, these techniques are used independently with pinch analysis limited to black-box representation of the regeneration network, which uses linear cost functions to account for wastewater treatment. However, detailed regenerator designs can be achieved with mathematical modelling, thereby capturing true regeneration cost.

The work presented in this dissertation, therefore, looks at the development of a systematic optimization framework that integrates graphical insights with mathematical modelling to reduce both model complexity and computational time. The graphical technique adopted in this work is Composite Table Algorithm (CTA), which is improved to determine an optimal regenerator removal ratio (RR) that simultaneously minimizes the freshwater requirement and wastewater generation within the water network. The improved CTA is demonstrated using literature examples for both fixed load and fixed flowrate problems. It is further adapted to solve a multiple contaminant problem using the reference contaminant approach. The mathematical model developed includes a detailed design of a reverse osmosis (RO) unit to allow for simultaneous optimization of water and energy used by the regenerator. This provides accurate cost estimation of the water network rather than the linear cost functions associated with the use of black-box representations in graphical targeting. Upon integrating the graphical and mathematical techniques in this study, results show that there was a reduction of about 85% in CPU time. This implies that the model converges faster and therefore favours the use of insight-based techniques as a preprocessing step for mathematical modelling.

Publications

The information presented below is the journal publication and conference presentation resulting from the work presented in this dissertation:

Journal publication

Mabitla, S. S., & Majozi, T. (2019). A hybrid method for synthesis of integrated water and regeneration networks with variable removal ratios. *Journal of Environmental Management, 231*, 666-678.

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List of Acronyms

ACTA	Automated Composite Table Algorithm
BOD	Biochemical Oxygen Demand
ED	Electrodialysis
FL	Fixed Contaminant Load
FO	Forward Osmosis membrane
FWR	Freshwater Region
HFRO	Hollow Fiber Reverse Osmosis
IP	Integer Programming
LCC	Limiting Composite Curve
LP	Linear Programming models
MEN	Mass Exchange Networks
MF	Microfiltration
MINLP	Mixed Integer Nonlinear Programming
MIP	Mixed Integer Programming
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
NNA	Nearest Neighbour Algorithm
NLP	Nonlinear Programming
OA	Outer Approximation
RLT	Reformulation Linearization Technique
RWR	Regenerated Water Region
RR	Removal Ratio
RO	Reverse Osmosis
RON	Reverse Osmosis Network

TAC	Total Annualized Cost
TOC	Total Organic Carbon
UF	Ultrafiltration
WCA	Water Cascade Analysis
WCT	Water Cascade Table
WUN	Water using network
WNS	Water Network Superstructure
WSL	Water Supply Line
WSD	Water Surplus Diagram

CHAPTER 1

Chapter 1 Introduction

1.1 Background

The need to protect the environment, as well as increasing freshwater and wastewater treatment costs have prompted industry to reduce freshwater consumption and wastewater discharge from industrial processes. Effluent treatment is necessary as industrial wastewater contains several contaminants such as total organic carbon (TOC), biochemical oxygen demand (BOD) and chemical oxygen demands, which can create environmental problems if discharged directly (Savelski & Bagajewicz, 2003). As a result, process integration is applied in industries for sustainable water management through exploiting opportunities of water reuse, recycle and regeneration. Process integration is a holistic approach to process design, retrofitting and operation that emphasizes the unity of the process and considers strong interactions that exist between the different unit operations (El-Halwagi, 2012).

In order to address the water network synthesis problem, two major approaches are used in literature, i.e. insight based techniques and mathematical modelling. The insight based techniques use the concepts of water pinch analysis. Water pinch is simply a systematic technique for analysing water networks and reducing expenditures of water consumption and wastewater treatments, through integration of different water using processes (Khezri, et al., 2010). Pinch analysis has been successfully applied in energy and emissions reduction (Klemes & Varbanov, 2013), resource conservation and sustainable design (Foo, 2012). Pinch technique was originally developed for the synthesis of heat exchanger networks (Linnhoff & Hindmarsh, 1983).

In the case of graphical targeting techniques, Wang & Smith (1994) are the earliest to apply water pinch analysis to solve a single contaminant water network with a fixed load framework. In their work, they explored process integration opportunities such as water reuse, regeneration reuse/ recycle in order to minimize freshwater and wastewater generation. Over the years, water pinch technique has been developed to cater for various problems of fixed load and fixed flowrate using advanced methods of graphical, algebraic and heuristic nature to solve the water network problem. Some techniques based on the pinch analysis concept include the water cascade analysis (Manan, et al., 2006), which is numerical alternative to the graphical water surplus diagram (Hallale, 2002). Recently, Parand et al. (2016) automated the Composite Table Algorithm (CTA) wherein interactions between key parameters such as pre-regeneration concentration and post-regeneration concentrations were explored to optimize the overall water network.

Although pinch based techniques are attractive for their simplicity and provision of conceptual insights, they are inherently limited to single contaminant systems (Hallale, 2002).The few researchers who attempted to cater for multiple contaminants using pinch based techniques include Gomes et al. (2013). This technique was improved by Calixto et al. (2015), who proposed a novel algorithm to predict and then remove concentration violations in unit operations. All these efforts are taken because there exist many contaminants in industrial wastewater and it is vital to eliminate most of them during wastewater treatment. On the other hand, mathematical optimization techniques are attractive for their capabilities in handling large scale problems with multiple operations and contaminants, as well as their ability to incorporate topological constraints in their formulation and provide accurate cost functions (Ahmetovica, et al., 2015).

The earliest work in mathematical optimization for water network synthesis was conducted by Takama et al. (1980). The model developed used nonlinear programming (NLP) with nonconvex bilinearities and nonlinear cost based objective function, which was minimized with a penalty on the discharge constraint. Moreover, other mathematical techniques for the water network synthesis include the work of Tan et al. (2009), who developed a nonlinear formulation that integrates a single, centralized partitioning regenerator with a source-sink superstructure for a single contaminant problem. However, the technique does not take into consideration piping interconnections cost. The formulation developed by Tan et al. (2009), was later improved by Khor et al. (2011) to incorporate multiple contaminants and include piping interconnections cost in the objective function. The proposed model consisted of a Reverse Osmosis Network (RON) formulation, continuous variables and binary variables for the piping interconnections all of which resulted in a mixed integer nonlinear programming (MINLP) model. The major challenges with mathematical optimization techniques are in their computational intensity and failure to provide physical insights to the resultant solution.

Therefore, the integration of graphical insights with mathematical optimization techniques has the potential of minimizing the challenges associated with the application of these techniques independently. The few researchers who integrated the techniques include Song et al. (2006), who combined the water-oxygen pinch analysis with mathematical programming for wastewater treatment. Additionally, Maria de Arruda et al. (2011) used the water surplus diagram (WSD) to support the GAMS optimization software in a process of differentiated regeneration. Although they used the results from the WSD to initialize their model, their work does not involve a detailed regenerator design and therefore fail to capture the accurate cost of the regenerator along with optimal cost of the water network.

1.2 Motivation

The motivation behind this work is that most works do not integrate the mathematical techniques with graphical targeting techniques in optimising the water network. However, such integration has the potential to offer rigorous designs for large scale water network problems within a short space of time. The few researchers who explored the integration of these techniques did not account for the Total Water Network, i.e. that which includes the individual elements of direct reuse/recycle, regeneration reuse/recycle and wastewater treatment, embedded with a detailed regenerator design. This is a significant gap in the field of water network synthesis because techniques which focused mainly on mathematical modelling were reported to consume large computational time to solve the water network. This is evident in the work of Buabeng-Baidoo & Majozi (2015), where the model converged after 54 hours to solve a water network with a detailed regenerator design. This large computational time was incurred upon allowing the model to determine an optimal removal ratio for a detailed reverse osmosis network (RON) superstructure within a multiple contaminant water network.

Moreover, there is limited research in the context of pinch based techniques on procedures which determine optimal regenerator performance prior the water network design. The performance of the regenerators is mostly predetermined for graphical techniques and this leads to suboptimal results. This is mainly due to the interdependence of freshwater use and regenerator performance within the integrated water network. Also, pinch analysis has been extensively applied to single contaminant problems rather than water networks of multiple contaminants problem in literature. This is despite the fact that industrial wastewater constitutes multiple contaminants in its nature.

In light of the above literature gaps, the work presented in this dissertation aims to develop a systematic optimization framework that takes advantage of the conceptual insights and rigor of mathematical modelling. The integration of these techniques is explored with the objective of reducing model complexity and computational time. Firstly, an Improved Composite Table Algorithm (CTA) is presented to design the water network with a partitioning type regenerator considering both single- and multiple-contaminant systems. The choice of CTA over other pinch based techniques was motivated by its ability to handle fixed load and fixed flowrate problems, its non-iterative nature and provision of both numerical accuracy and physical insights (Agrawal & Shenoy, 2006). To the best of our knowledge, CTA has never been applied to handle multiple a contaminant water network embedded with a partitioning type regenerator of unknown performance. Next, the flow targets and optimum removal ratio (RR) obtained from the Improved CTA provides initial information for solving the mathematical formulation of the water network with a detailed reverse osmosis (RO) regeneration unit. By incorporating the Improved CTA as the pre-processing technique for the mathematical formulation that is solved using selected solvers in a GAMS platform, this research aims to achieve optimal water network models with faster convergence. Although a generic linear cost function is applied for the blackbox regenerators in graphical targeting technique, accurate regeneration cost which quantifies the amount of energy utilized is determined in this work using mathematical modelling.

1.3 Objectives

The objective of this work is to determine an optimum removal ratio of the embedded regenerator using a graphical approach, which will simultaneously give minimum wastewater generation and freshwater requirement. In addition, develop a systematic framework that integrates graphical insights with mathematical modelling, to develop a complete water network superstructure with a detailed water regeneration unit.

1.4 Problem statement

This work addresses the problem of optimizing water networks for both fixed load and fixed flowrate problems. A fixed load system is one in which operations use water as a washing agent to remove a fixed amount of load. The fixed load problem can therefore be stated as follows:

Given:

i) A set of processes, P, with known limiting water flowrates, F_P.

ii) Information about the maximum inlet concentrations, ${C_{Pin,x}}^U$, and outlet concentrations, ${C_{Pout,x}}^U$, from the processes.

iii) A fixed amount of load, $M_{P,x}$, that must be removed from the processes.

iv) A single regenerator with maximum inlet concentration of ${C_x}^U$ and liquid recovery, α.

On the contrary, a fixed flowrate system is quantity controlled rather than quality controlled and the mass load is allowed to vary. In this context, the problem statement for the fixed flowrate problem can be stated as follows:

Given:

i) A set of water sources, J, with known flowrates, F_j, and known contaminant concentrations, $C_{j,x}$. A freshwater source with variable flowrate and known contaminant concentration, C_x, forms part of these sources.

ii) A set of water sinks, I, with known flowrates, F_i, and known maximum allowable contaminant concentrations, ${C_{i,x}}^U$. In addition to this set is a wastewater sink with variable flowrate and known contaminant concentration limit, C_e. Note that C_e is equivalent to the environmental discharge limit concentration.

iii) A single regenerator with maximum inlet concentration of ${C_x}^U$ and liquid recovery, α.

Determine:

(i) The optimal removal ratio (RR) using a graphical approach, that minimises both freshwater and wastewater generation within the water network.

(ii) The optimal configuration of the water network with a detailed design of the regeneration unit (reverse osmosis membrane, RO)

1.5 Dissertation Structure

The dissertation is arranged from Chapter 1 to Chapter 6. In Chapter 2, a comprehensive literature review is provided on the different techniques for water network synthesis. In particular, this covers literature on approaches such as insight based techniques, mathematical modelling and lastly the integration of these techniques. Chapter 3 covers the methodology proposed for the integrated framework. In Chapter 4, the applicability of the proposed systematic technique is demonstrated using three literature examples and an industrial case study of a water fabrication plant. Then Chapter 5 covers the recommendations and considerations for future work. Lastly, conclusions are presented in Chapter 6. Also, each chapter is followed by a list of references and the journal paper published for this work is attached at the end of this dissertation

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Chapter 2 Literature Review

2.1 Introduction

The work in this dissertation focuses on the integration of a pinch based technique (CTA) with mathematical modelling. A succinct background on the application of these different techniques for freshwater and wastewater minimization is brought into contention herein. Moreover, the advantages and disadvantages of these network optimization techniques are discussed to highlight the importance of using the improved CTA to preprocess mathematical modelling.

The motive behind integrating the techniques is to reduce model complexity and consequently the computational time. This is because the incorporation of a detailed RON in the water network results in a complex MINLP framework. The complexities associated with solving this model arise from the existence of bilinear terms (which create mass balances equations of nonconvex functions), binary variables and concave cost terms in the objective function (Ahmetovic & Grossmann, 2011). An introduction to membrane technology is given along with the design principles of a Reverse Osmosis Network.

In this section of this work, the different techniques found in literature to solve the water network synthesis problem both dependently and independently, are examined. Also, the different techniques used to preprocess mathematical modelling are also reviewed along with the techniques developed in literature for the hybrid or integrated system for water network synthesis.

2.2 Water network synthesis

Water is an important resource used as a reagent, washing or cooling agent and product transportation medium in various industrial sectors such as pharmaceuticals, mining, petrochemical and petroleum sectors. The synthesis and retrofit of water networks with either continuous or batch operations is referred to as the water network synthesis problem (Khor, et al., 2014). In essence, the synthesis problem can be solved through optimal combination of schemes of direct reuse/recycle and regeneration. The water network problem comprises of; water-using units (also referred to as sinks), water sources and wastewater treatment operations (also called regenerators). Moreover, freshwater sources, wastewater disposal sites, mixers and splitters are all other elements of the water network (Jezowski, 2010). The water network is designed by taking into account limiting data for each operation, i.e. fixed mass load to be removed for each unit; the maximum inlet and outlet concentrations for the sinks and sources, respectively. The integration of sources, sinks and regenerators lead to a total water network design, that which is achieved through optimization of the objective function. In this regard, the objective function minimizes the freshwater requirement, ensures wastewater discharge at acceptable environmental standards and reduces the water network capital costs.

2.2.1 Features of the water network

The water-using units or sinks require water or use water from sources and regenerators. Amongst the sinks is a wastewater sink, which has a maximum inlet concentration that is in compliance with the environmental regulations. Water sources produce water or discharge effluent to sinks, regenerators or waste sites. Freshwater forms part of the water sources and usually has an unknown flowrate, which is determined upon optimization. The water-using units can be subjected to mass transfer limitations or operate as non-mass transfer units. Mass transfer operations use water as a washing agent and are referred to as quality controlled or fixed load operations while non-mass transfer operations are known to be quantity controlled or fixed flow-rate operations (Jezowski, 2010). In the case of a fixed load problem, operations are characterized by both maximum inlet and outlet concentrations while the flowrate through the units can be less or equal to the limiting flowrate. On the contrary, non-mass transfer operations are characterized by both fixed outlet concentration and fixed flowrates. Therefore, these operations may have different inlet and outlet flowrates which may bring about water losses or gains around a specific operation. Some examples of the mass transfer operations include extractors and separators while reactors and distillation columns form part of non-mass transfer operations.

In addition, there are techniques developed in literature for the conversion of fixed load processes to fixed flowrate processes and vice versa. The former conversion is achieved by dividing the fixed load operations into process sources and sinks, through setting their concentrations to a maximum with the objective of minimising the freshwater requirement (Poplewski, et al., 2010). On the other hand, the conversion of fixed flowrate process to fixed load is applied under the assumption that the sinks initially receive an infinite amount of load (Agrawal & Shenoy, 2006). This assumption is relaxed upon the introduction of sources in the system to generate a Limiting Composite Curve (LCC). The detailed application of the fixed flowrate conversion to fixed load processes shall be demonstrated in the methodology section of this treatise under the improved CTA technique. It is noteworthy that previous studies successfully performed this conversion focusing only on single contaminant systems. As a result, it shall be demonstrated in this work that CTA can be improved to cater for multiple contaminants, using the reference contaminant algorithm by Calixto et al. (2015). Note that all these efforts are undertaken to benefit from the versatility of the fixed flowrate techniques, which caters for practical water losses and gains common with real industrial processing units.

Furthermore, the water network synthesis problems can be isothermal or non-isothermal. The isothermal networks are assumed to have streams of constant temperature while the non – isothermal networks incorporate temperature changes which occur as a result of stream mixing, heating or cooling to meet process requirements (Ahmetovica, et al., 2015). The scope of this study is however limited to the optimization of isothermal process water networks. This is because there are more stringent environmental regulations imposed on the contaminant concentration of the discharged wastewater rather than the effluent temperature. The reader is referred to Ahmetovica et al. (2015) for a comprehensive review on studies which address issues of heat-integrated interplant water networks.

Moreover, the regenerators in the water network can perform partial treatment of wastewater using processes such as membranes filtration, stripping or chemical additives. The regenerators can be centralized or decentralized within the water network. The centralized wastewater treatment refers to an end-of-pipe type of treatment where all wastewater streams are merged into one stream before being fed to the treatment unit (Chew, et al., 2009; Tan, et al., 2009). However, this type of treatment is capital intensive as the feed to the regenerator is highly concentrated and the quantity is usually larger. On the other hand, distributed wastewater treatment involves separate treatment of streams or their partial mixing upon feeding a treatment unit (Wang & Smith, 1994b; Galan & Grossmann, 1998). This approach reduces both the wastewater mass load and quantity, thereby resulting in reduction in both capital and operating costs. All these efforts are explored with the objective of minimizing freshwater use in operations as the regenerated water can be re-used in the water network and the regenerator effluent can be discharged into the environment at acceptable concentration levels.

These wastewater treatment units are necessary in order to meet acceptable effluent discharge standards to the environment and consequently reduction in the grey water footprint. In simpler terms, the grey water footprint indicates the quantity of freshwater required in assimilating pollutants in wastewater to meet environmental discharge limits (Hoekstra & Mekonnen, 2012a). Therefore; opportunities of water reuse, regeneration reuse and recycle are employed in industries for sustainable development in order to avoid penalties associated with con-conformance to environmental limits. These freshwater and wastewater minimization opportunities are to be examined in the subsequent section.

2.2.2 Freshwater and wastewater minimization schemes

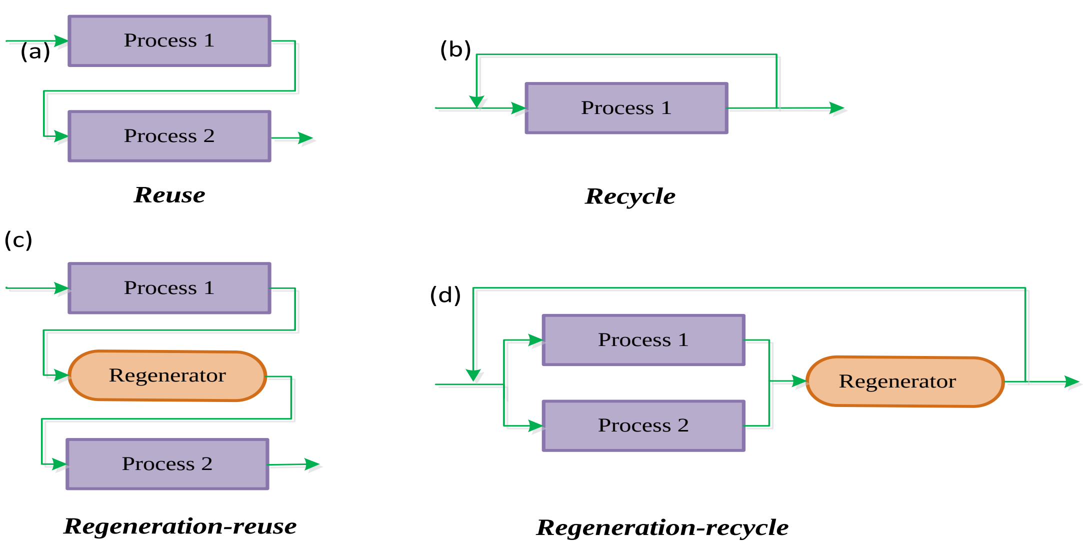


Figure 2.2.1 Various schemes for water reduction: (a) reuse, (b) recycle, (c) regeneration-reuse, and (d) regeneration-recycling (Kuo & Smith, 1998)

The different process integration scheme are necessary for water network cost optimization and operational efficiency. In reference to Figure 2.2.1 above, direct water reuse involves the reuse of effluent from one source into other operations with consideration on the maximum inlet concentration of the sources. This is because by adhering to maximum limits of other operations, concentration violations are avoided and mass load feasibility is ensured. On the other hand, direct recycle involves the feeding of effluent from one process back to the same process, whilst regeneration reuse involves partially treating water from a source to qualify it for reuse in other processes. This qualification is in terms of concentration levels as the objective is to not exceed limits put on other operations. Lastly, regeneration recycle involves partial treatment of effluent to remove contaminant build up in operations and then recycling of the regenerated water to the same operations.

2.3 Challenges and solutions to the water network synthesis problem

2.3.1 Background on optimization

In water networks, a mathematical model is formulated on the basis of a superstructure representation of all possible combinations between sources, sinks and wastewater treatment unit. This model is composed of mathematical relationships of equations, inequalities and logical expressions which describe the overall system and take into account all constraints of; economics, geography, safety and system control. In engineering, optimization is a critical step that follows a mathematically described problem. This approach leads to sustainable and optimal designs at lower costs. In essence, optimization refers to the process of determining the best solution to a mathematically defined problem, through minimizing or maximizing an objective function that is subjected to a set of equality and inequality constraints (Liberti, 2008; Snyman, 2005). The classification of optimization problems can be summarized in Figure 2.3.1 below:

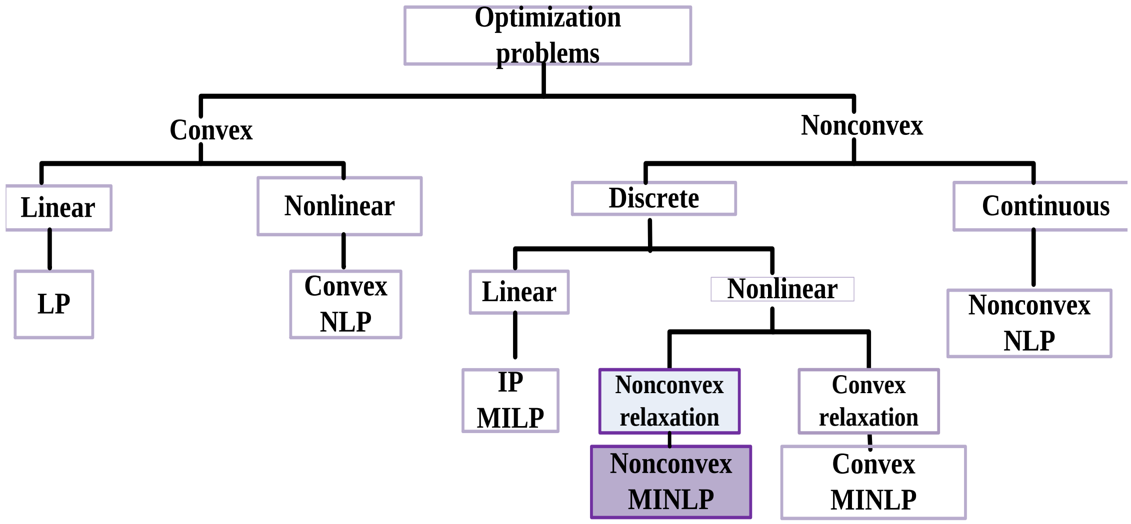
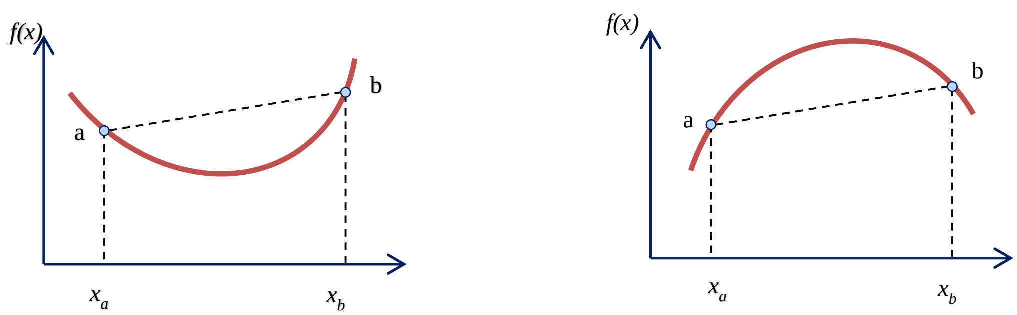


Figure 2.3.1 Types of problems related to the optimization problems (Lin, et al., 2012).

As illustrated in Figure 2.3.1 above, the optimization problem can be divided into convex and nonconvex problems. The nonconvex problems are complex in nature and are not solvable with the available algorithms in literature. These types of problems result in many suboptimal solutions or local optima (Zamora & Grossman, 1998) and global optimal solutions cannot be achieved with the existing local optimization models (Ryoo & Sahinidis, 1996). On the other hand, convex problems or those belonging to a class of generalized convexity, guarantees the approximation of a global optimum (Horst, 1984). The diagrammatic distinction between convex and concave function is illustrated in Figure 2.3.2 below:



(a) Convex function

(b) Concave function

Figure 2.3.2 The graphs of convex and concave functions

To further describe the models in Figure 2.3.1 above, optimization problems which consist of linear equality and inequality expressions are called Linear Programming models (LP). A nonlinear programming model (NLP) is a result of the existence of a nonlinear constraint or objective function. Additionally, integer programming (IP) models results from specifying any of the variables as whole numbers. In the presence of a combination of discrete and continuous variables, the IP model can further be called a mixed integer programming model (MIP). Moreover, an MIP model that is linear and one which is nonlinear are called mixed integer linear programming (MILP) and mixed integer non-linear programming (MINLP) models, respectively. However, the water network superstructure with a regenerator embedded in it, contains binary variables, bilinear terms (products of continuous variables or products of binary with continuous variable) in the mass balance terms and concave cost functions, thereby resulting in a non-convex MINLP model formulation. The binary variables account for the topological constraints, the existence of units, streams, and piping interconnections. The MINLP model formulation is computationally intensive and requires robust algorithms to achieve an optimal solution.

An optimal solution is the best solution to an objective function and is achieved from a set of feasible solutions (Edgar & Himmelblau, 1988). A feasible solution in an optimization problem is attained when the constraints of the problem are satisfied by the variables set (Edgar & Himmelblau, 1988). This solution is found within a feasible region along with other possible feasible solutions. However, there exists different types of optimal solutions and this is dependent on whether the objective function is convex or nonconvex. Furthermore, a function can be strictly convex and/ strictly concave. The former differs from the conventional convex function by the greater-than sign, which replaces the greater or equal to sign. The latter replaces the less or equal to sign in the concave function with just a greater-than sign. This implies that, only a single optimal solution is achievable with strictly convex or concave functions (Edgar & Himmelblau, 1988).

In light of the above discussion, convex functions are ideal for the model convergence to near optimal or globally optimal solutions. Therefore, an optimal solution can be classified into; local maximum, local minimum, global minimum or a global maximum solution. The global minimum or maximum is regarded as the best solution to an optimization problem and is therefore desired or targeted in mathematical optimization problems. Due to the complexities that arise with superstructure optimization of the water networks, the models formulated are in most cases nonlinear and nonconvex. This led to an exhaustive search in literature for different rigorous algorithms and solution procedures for relaxation and linearization of superstructure optimization problems. These procedures along with challenges in water network synthesis are brought into contention in the subsequent section.

2.3.2 Challenges in water network synthesis

Due to the detailed mathematical formulation of the water network problem, the optimization models are usually complex and susceptible to a number of issues such as nonlinearity, uncertainty and nonconvexity (as already explained in the previous section). Nonlinearity is mostly stimulated by the incorporation of a detailed regeneration unit into the water network. This is because regenerators are inherently nonlinear and complex computationally intensive models may result from their integration with the water network. In reference to the work of Abbas & Majozi (2016), the resultant model for water network embedded with a detailed regenerator is approximately 84% computationally higher than the black box regenerator model incorporated within the water network. This is because linear cost functions are used for the black box regenerator and fast convergence is achievable for such models.

Moreover, uncertainty in mathematical modelling is another major challenge for water network synthesis. Optimization under uncertainty refers to cases where the model to be solved involves uncertain data or estimated parameters and this is known as stochastic programming or stochastic optimization problems (Diwekar, 2003). The issues of uncertainty arise from the existence of system parameters within mathematical models, which are unknown in nature and require some estimation prior to solving the problem. In the waste management and water resource management sectors, these forms of uncertainty include unknown parameters of waste generation rates, operation cost, transportation cost waste loads or disposal capacities and basic indicator values (Verderame, et al., 2010).

Nevertheless, there are various approaches in literature for formulating water network synthesis models under uncertainty and these include stochastic programming, robust optimization, stochastic optimal control (Cheng, et al., 2004). However, robust optimization is adopted in this research due to its strength to guarantee that the solution obtained is feasible for the nominal set of system conditions and robustness in terms of the different forms of parameter uncertainty within the network (Ben-Tai & Nemirovski, 1998). Lastly, procedures to tackle the challenges of non-convexities within the water network are contextualised in the subsequent section.

2.3.3 Relaxation and decomposition techniques for complex mathematical models

The issues of non-optimality and limitations of most local optimization models to solve nonconvex function, have led to vast research on direct linearization techniques (Zamora & Grossman, 1998). These techniques include generating a "good" starting point, using sequential solution procedures and using global (deterministic) optimisation methods.

i) Generation of a good starting point:

Global optimum or good optimal solutions can be achieved with this technique through the use of problem linearization methods. In the field of water minimization, this technique helps remove bilinear terms through fixing the outlet concentrations in unit operations to their maximum allowable values (Jezowski, 2010). A good starting point in mathematical optimization is essential especially for deterministic and stochastic optimization due to their contribution to higher rates of model convergence or short CPU time (Zamora & Grossman, 1998; Poplewski, et al., 2010). Moreover, a good starting point increases the chances of local solvers achieving optimal solutions of high quality, thereby alleviating their vulnerability to being trapped into suboptimal solutions due to poor starting points (Teles, et al., 2008)

Authors such as Galan & Grossmann (1998) attempted to find a good initial point for a multiple contaminant wastewater network. The resultant formulation of the wastewater treatment model was a nonconvex nonlinear problem. This type of problem is associated with solutions of local minima and convergence challenges requiring suitable initialization. In order to tackle the aforementioned modelling issues, the authors proposed successive solutions of the relaxed linear model and the original nonconvex nonlinear problem.

Firstly, NLP model which consists of nonlinear bilinearities in the mixer unit of the distributed wastewater treatment was formulated. Secondly, an MINLP model was built wherein the selection of different treatment technologies was explored through the incorporation of a binary variable in the formulation. Amongst the different starting points, (due to different objective functions) obtained from the relaxation of LP model, the best solution was selected and set as the lower bound or starting point for the NLP model. Although the determination of a good starting point has the potential to increase the convergence of both the NLP and MINLP models and therefore reach global optimal solutions, the method used was computationally intensive.

In addition, Li and Chang (2007) developed an initialization strategy to solve both NLP and MINLP models for water networks with multiple contaminants. The initialization was built on knowledge about each unit's water losses, the maximum inlet and outlet concentration of contaminants around each unit and the mass load to be removed (Li & Chang, 2007). The initialization successfully estimated near optimal solutions at shorter computational times but is limited to small scale problems and global optimality cannot be guaranteed.

Moreover, authors such as Teles et al. (2008) developed an initialization technique for the design of a water network without a wastewater treatment unit. In this work, the NLP is replaced with a succession of LP models that are then tackled for all the different substructures of the operation sequences (Teles, et al., 2008). The generation of multiple starting points with this procedure increases the chances of obtaining global optimal solutions rather than standard initialization techniques which generates a single starting point. However, the sequential nature of the procedure eliminates some parts of the feasible region and was found to be computationally expensive.

ii) Solution sequence

In this procedure, outlet concentrations are fixed at their maximum and slack variables are incorporated in the MILP formulation to relax the constraints in the material balance. In the generation of the water network superstructure (WNS), Gunaratnam et al. (2005) proposed a three staged procedure to initialize the MINLP model for a water network with wastewater treatment. Firstly, relaxation of material balance is performed by allowing maximum outlet concentrations in unit operations and introducing slack variables. This was done with the objective of creating an MILP formulation. Then, the flowrate solutions provide initialization for the LP model which then creates concentrations for the MILP model. In the LP problem, the aim is to minimize the sum of slack variables introduced in the initial stage. Then finally, the MILP-LP solution performs initialization of the overall MINLP model. In this stage, the solution of the MINLP formulation is achieved through the convergence of the sum of slack variables to a very small number. In order to reduce the complexity of the network, Gunaratnam et al. (2005)

specified minimum flowrates, piping costs and number of streams mixed together. However, this technique is computationally demanding due to its iterative nature. Moreover, global optimality cannot be guaranteed in this work and there was no detailed design of the wastewater regeneration unit.

Furthermore, Doyle & Smith (1997) developed an iterative procedure for targeting maximum water reuse within the water network. This is a sequential method wherein superstructure optimization is conducted through initializing a non-linear optimization model with a linear model. In order to formulate the LP model, the mass transferred within the water using operations is modelled by fixed outlet concentration while the non-linear model is characterized by fixed outlet concentration (Doyle & Smith, 1997). Although global optimality cannot be guaranteed with this approach, the authors successfully achieved model convergence through the addition of some slack variables to relax the inequality concentration balances.

iii) Deterministic methods

Deterministic global optimization techniques use convex relations to attain global optimal solutions or solutions near optimal for nonconvex problems. These relations, as presented by McCormick (1976), of over and under estimators, are used along with global optimization techniques to converge problems of nonconvex MINLP formulations. In deterministic modelling, there are initial conditions and parameters which are set to determine variables and also influence model convergence. According to Lin et al. (2012), deterministic approaches can generate sequence of points that converge to a global optimum by taking advantage of the mathematical structure or analytical properties of the problem. The different approaches used to achieve global optimality in optimization problems include linear programing, non-linear programming and mixed-integer nonlinear programming. The MINLP model is solved using sub-solvers to break down the model into subsections to effect model convergence to a global optimum solution. There are different optimization solvers such as LINDO and Baron, which can provide a platform for the optimization procedure. However, the size and complexity of the problem determines the appropriate solver to use. The optimization procedure consists of spatial branch and contact algorithms for NLP model, branch and bound framework to reduce algorithms or handle binary variables and lastly piecewise underestimators and overestimators (Quesada & Grossmann, 1995). The following are the different deterministic global optimization methods;

(a) Branch and bound

The branch and bound method was first proposed by Land & Doig (1960) for discrete programming. There are various solvers which use the branch and bound method to find solutions to optimization problems and these include Cplex, standard branch and bound, SBB and Lindo/LindoGLOBAL, (GAMS Development Corporation, 2013). This method is performed over a feasible domain of a continuous/ discrete variable that is divided successively into subregions within a particular search space. In this method, the successive subdivision of the feasible domain is referred to as branching while bounding is the computation of the lower and upper bounds obtained from these regions. There are lower and upper bounds of optimal values of the objective function which are generated within these subregions. There is a relaxation gap that results from the difference between the lower and upper bound. This gap is used as a basis to evaluate the extent to which the upper bound is closer to global optimality. Therefore, there are iterative procedures conducted to ensure that the relaxation gap is within an allowable tolerance. During the iterative procedure, subregions which have their lower bounds inferior to the upper bound are deleted from the search. This iterative procedure results into a tree structure with a pyramid of subproblems (Ryoo & Sahinidis, 1996).

There are different branch and bound techniques available in literature and these are distinguished based on whether branching is conducted on discrete or continuous variables and also on the tightening of the lower and upper bounds (Grossmann & Biegler, 2004). Some schemes perform spatial tree enumeration on both discrete and continuous variables, wherein there is reduction in the domains of the variables to achieve tighter relaxations that eventually converge to global optimality. There are schemes that branch on the continuous variables while others branch on discrete variables and switch to spatial branch and bound at the nodes to guarantee feasibility (Grossmann & Biegler, 2004).

Additionally, there are two different approaches that are used to perform the branching technique. These are the depth-first and breadth-first approaches, whereby the former conducts branching on the most recently created nodes within the tree while the breadth-first approach selects a node with the best value at each level and expand on all its successor nodes. The depth-first approach is attractive for its feature to analyze only fewer nodes, thus less storage requirement as backtracking to shallower nodes (which are less likely to yield valid solutions) is not forced. This contributes to faster convergence to an optimal solution early in the enumeration procedure compared to the breadth-first approach (Ryoo & Sahinidis, 1996).

(b) Branch and reduce

Branch and reduce algorithm is another pre-processing technique for global optimization problems. This algorithm has been used in literature to improve the performance of the branch and bound technique, particularly the bounding procedure of the technique (Sahinidis, 2003). The traditional branch and bound is advanced through analyzing constraints, interval arithmetic and duality to draw conclusions regarding ranges of integers and continuous variables (Sahinidis, 2003). The application of the reduction technique to every sub-problem of the search tree will help contract the space and reduce the relaxation gap. This approach eliminates infeasible sub-regions by applying feasibility and optimality criteria. The feasibility based techniques eliminate the infeasible parts of the nonconvex problem through an iterative mechanism that uses structures of the variable bounds and constraints. On the other hand, convex relations form the basis for carrying out elimination of infeasible regions of the objective function for the optimality based techniques (Zamora & Grossman, 1998).

The branch and reduce algorithm is applicable in a global optimization solver called BARON, wherein branching is conducted on both continuous and discrete variables (Grossmann & Biegler, 2004). The models built in BARON usually require additional constraints and some finite bounds (lower and upper) on certain variables in order to achieve both optimality and convergence within a reasonable time interval. The solution process steps that BARON follows are summarized in Figure 2.3.3.

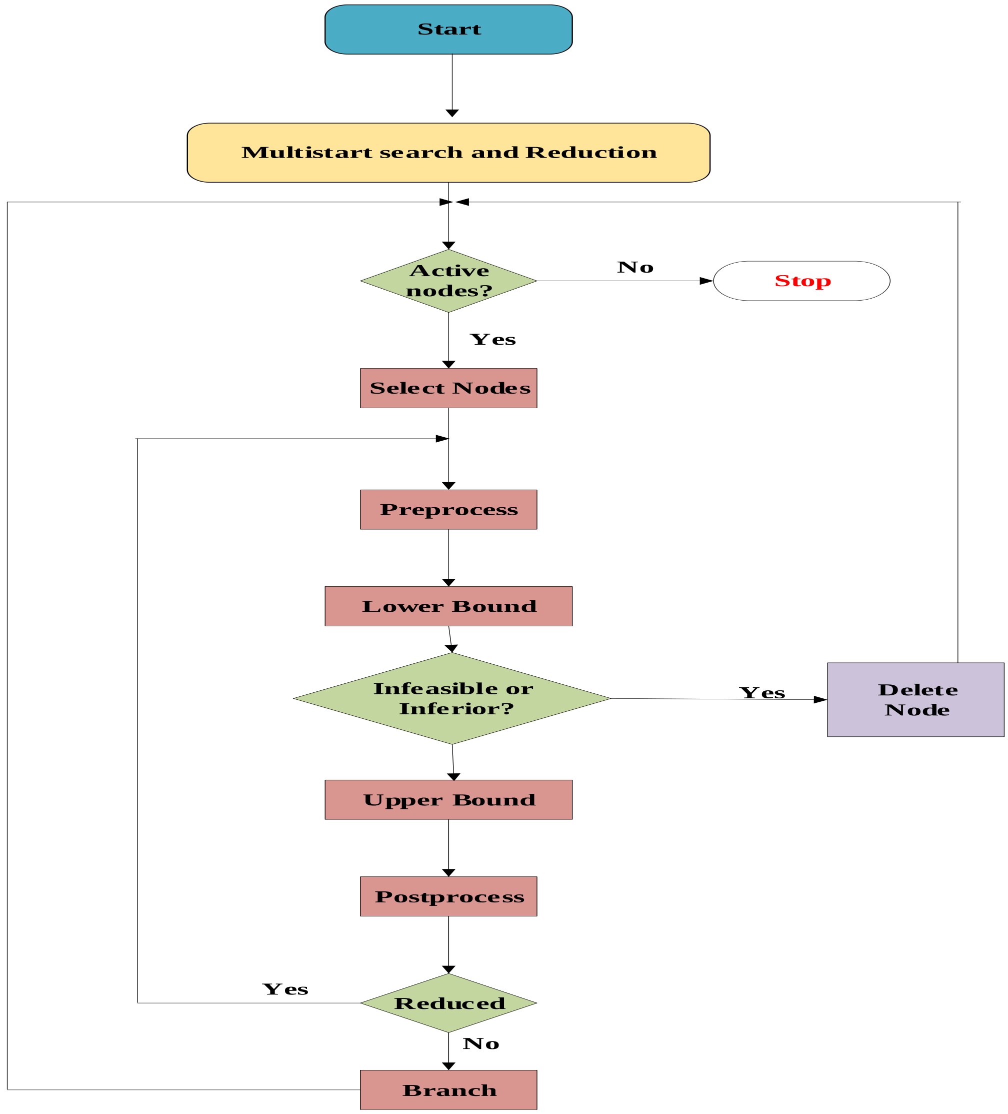


Figure 2.3.3 The algorithm for Baron

In most research work, BARON is used for global optimization and the algorithms frequently incorporated within the solution procedure include Branch & Bound and Branch and Reduce methods (Grossmann & Biegler, 2004). A few of these techniques include the work of Zamora and Grossmann (1998) who formulated a wastewater treatment network superstructure that resulted into a MINLP model. The representation of their water network was of a fixed load type and the network was solved for a multiple contaminant system. In this case BB was used along with bound contraction procedure. Then authors such as Koppal & Bagajewicz (2003) used BB with Cplex to solve their single contaminant and fixed load water network that resulted into a MILP model formulation. Lastly, Karuppiah and Grossmann (2008) used BARON with DICOPT to solve their total water network synthesis/ retrofit which resulted into a NLP and MINLP model formulation.

(c) Cutting planes method

Convex optimization problems can be solved using the cutting planes method by generating integer solutions through a series of relaxations. The feasible sets of these relaxations are tightened through the successive addition of valid cuts or linear inequalities improved from the generated polyhedral outer approximation (Duran & Grossmann, 1986). The optimal value is found from the convergence of the lower and upper bounds of the optimal value during the iterative cutting planes method. The few techniques which are categorized under the cutting planes method include outer approximation method (OA), extended cutting planes and benders decomposition method (Nowak, 2005).

In the case of the outer approximation method, convex or concave functions are applied along with convex sets to approximate a function through a polyhedral that contains these sets. In essence, the outer approximation (OA) technique which was first introduced by Duran and Grossmann (1986), uses piecewise linear functions to approximate a function. The procedure involves successive iterative linearizations which generate an upper and lower bound on an MINLP solution. The solver platform used is DICOPT (Lee & Leyffer, 2012), wherein the problem is divided into the major MIP (under which integer variables are fixed) and minor NLP subproblems (under which linearization is carried out through OA methods). The DICOPT solver terminates under cases where further iterations do not improve the NLP solution and this often implies that the solution is trapped as local optima, especially for problems of nonconvex functions. The illustrative diagram for outer approximation method is represented in Figure 2.3.4 below.

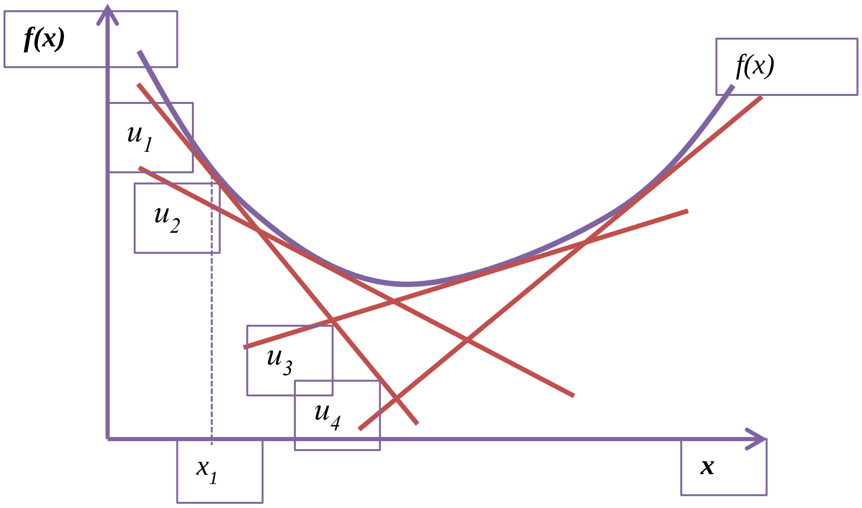


Figure 2.3.4 Outer approximation representation (Duran & Grossmann, 1986)

As depicted in Figure 2.3.4 above, the representation of the outer approximation procedure forms a convex function that underestimates and overestimates the objective function and the feasible region, respectively. It can be deduced from Figure 2.3.4 that the approximation is performed at four different points which are represented by the different slopes (or lines) from u_1 to u_4, with x_1 given as the starting point. Although outer approximation is widely used to solve mathematical optimization problems, it requires a large number of approximations to achieve an adequate approximation and that makes it computationally intensive.

iv) Direct linearization

Non-linear terms in the mathematical models are linearized to reduce the complexity of the model. Researchers such as McCormick (1976) introduced a linearization method for concave and convex envelops of the functions. Although applying convex relations to relax the bounds reduces computational difficulties, the optimal solution in the relaxed problem will not always be the optimal solution to the objective problem. Therefore, McCormick method does guarantee convexity but with a disadvantage of achieving sufficiently tight bounds (McCormick, 1976). Other techniques to linearize the water network superstructure (WNS) were developed for both single and multiple contaminants. These techniques include the optimality conditions developed by Savelski & Bagajewicz (2000; 2003) for linearizing the water network. The schematic representation of this typical water network with different process units is depicted in Figure 2.3.5 below:

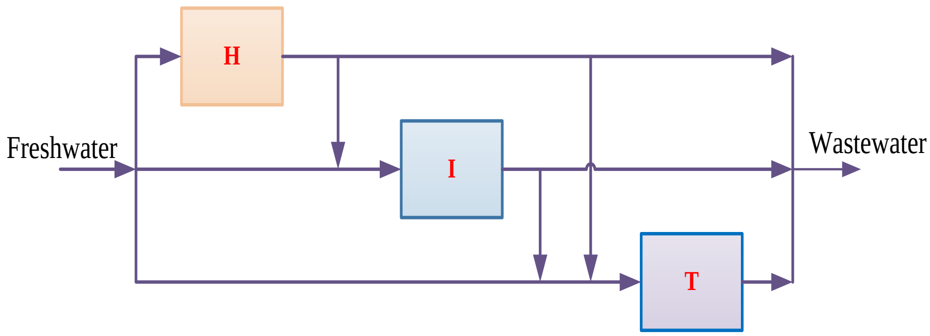


Figure 2.3.5 Schematic representation of the water network (Savelski & Bagajewicz, 2003)

Where, H - refers to head process, I - stands for intermediate process and T – stands for terminal process. The optimality conditions are explained below in reference to Figure 2.3.5 above:

- **Concentration monotonicity condition**: This means that the outlet concentration from a process must be greater or equal to the combined concentrations of all preceding processes. In the case of a multiple contaminant problem, the key contaminant must follow this condition.
- **Maximum outlet concentration condition**: The freshwater using processes which require their outlet concentrations to be maximum are the head processes (H). Therefore these processes can only be fed by freshwater. In addition, intermediate processes (I) are fed by wastewater from other processes and discharge it while the terminal processes (T) only discharge their wastewater for treatment and not to any process. However degenerate solutions with lower outlet concentrations may occur in these processes, increasing flowrates in other processes (Savelski & Bagajewicz, 2000).
- **Regenerator outlet concentration**: the outlet concentration of a regenerator must be as small as possible.

It is worth noting that the above optimality conditions are formulated under the assumptions that; each water-using operation has the following:

i) A fixed mass load that needs to be removed, and is,

ii) Characterized by maximum inlet and outlet concentration constraints.

In summary, linearization techniques have been proposed in literature to simplify complex mathematical models. In reference to the above discussion, mathematical optimization tools with appropriate initialization techniques can solve complex single or multiple contaminants problems. Moreover, such optimization tools can simultaneously achieve targets of minimum flowrates and designs of optimal water network. In the subsequent sections, graphical and mathematical techniques which have been developed in literature to solve the water network synthesis problem are examined. These efforts are undertaken with the objective of minimizing industrial water consumption, managing wastewater discharge with considerations on environmental regulations and thereby alleviating wastewater discharge penalties. Furthermore, research work which integrated the insight-based techniques with mathematical modelling are reviewed in the last section of this treatise.

2.4 Approaches for water network synthesis

The approaches which can be used to synthesize the water network are the; insight based techniques, the mathematical optimization based techniques and the integration of these techniques (hybridization of insights and mathematical modelling).

2.4.1 Insights based techniques

The well-developed graphical technique that has been used over the years for water network synthesis is water pinch analysis technique. Water pinch is simply a systematic technique for analyzing water networks and reducing expenditures that are associated with different water-using operations (Khezri, et al., 2010). Water pinch comprises of both targeting and design stages, with the former necessary for setting targets for minimum freshwater and wastewater flowrates while the latter involves matching of process units (sources and sinks) to meet the set targets. The main envisioned goal of performing pinch analysis in a water network is to solve the mass integration problem. This is achieved by transferring contaminant mass load from a rich stream to a lean stream, while simultaneously reducing wastewater and freshwater flowrates. The following sections provide some detailed background on water pinch targeting techniques; with emphasis on the techniques developed for water-reuse/recycle, regeneration reuse/recycle, wastewater treatment, total water network and lastly multiple contaminant water networks.

i) Targeting techniques for water re-use/recycle

The first work in pinch analysis was done on heat exchanger network for energy efficiency (Linnhoff & Hindmarsh, 1983). In their methodology, both energy and utilities within the heat exchanger were minimized simultaneously with a reduction in the number of required heat exchanger units. This technique contributed to higher energy recoveries with minimum capital expenses. The concept was then adopted for mass exchange networks (MEN) where the pinch point was used as the basis for the network design (El-Halwagi & Manousiouthskis, 1989). Their technique maximized the amount of species transfer between the rich and lean streams, thus improving on the configuration on the MENs. Then, Wang and Smith (1994) developed a graphical technique that represents contaminant concentration versus mass load. This technique is well known as the Limiting Composite Curve (LCC), which is an overall representation of the water network. The construction of this curve involves generating a plot of mass load (on the x-axis) and contaminant concentration diagram. In principle, the mass load of all operations is accumulated within each concentration interval. The main objective of such a set-up is to locate a pinch point, which is the point of interception of the limiting composite curve and the water supply line. The water supply line is a plot that begins from the origin of diagram and rotated until it intercepts a single point on the LCC. Deduced from the diagram is that operations below the pinch require some freshwater and those above the pinch can reuse water from other operations to remove their contaminant load. The following information is used to determine the limiting data for each unit (Wang & Smith, 1994):

- mass transfer behaviour
- solubility limits
- need to avoid precipitation
- fouling and corrosion limitations
- flowrate limit to avoid solid material settling

Furthermore, Kuo and Smith (1998), expanded on the aforementioned technique through the incorporation of water mains which may act as sources or sinks depending on their position in the water network. Firstly, a freshwater target was obtained through locating the pinch point as observed in Figure 2.4.1 below. Then design grids were set and water operations were connected to water-mains which depict the targeted water requirement (90t/h) at the top and the generated wastewater at the bottom, as depicted in Figure 2.4.2.

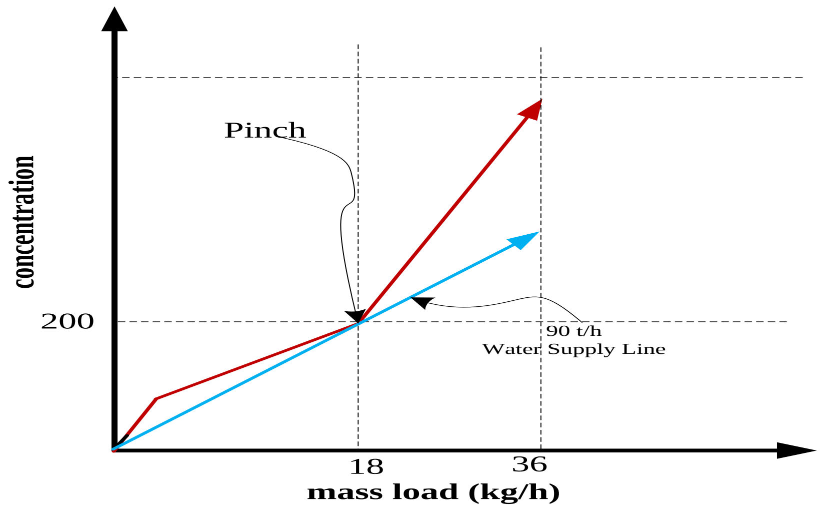


Figure 2.4.1 Limiting water profile and limiting composite curve (Kuo & Smith, 1998)

However, the above discussed techniques have limitations such as inability to identify minimum freshwater and wastewater for multiple sources, sink and contaminants and cannot cater for operations with water losses. In addition, geographical distances and safety constraints are not incorporated in the above procedures, thus limiting their feasibility (Doyle & Smith, 1997). Furthermore, these approaches were found to be limited to mass transfer operations (Mehrdadi, et al., 2009), rated tedious, largely dependent on designer's experience and tend to omit integration opportunities between sinks and treatment units within the water network.

An attempt to eradicate the above limitations was conducted in the work of Dhole et al. (1996). These authors proposed a graphical technique that uses concentration versus flowrate to calculate supply and demand composite curves. The technique catered for both FL and FF problems and was termed the Source-Sink Composite Curves method. Their approach had proven to be successful in accounting for multiple contaminants. In this technique, freshwater minimization and wastewater reduction targets were achieved by not using fresh water above the pinch and discharging sources above the pinch point as wastewater. On the other-hand, it failed to eliminate multiple pinch points that may occur due to mixing of water sources, which altered shape of the source composite curve, thus yielding inexact calculations of freshwater and wastewater generated in the water network.

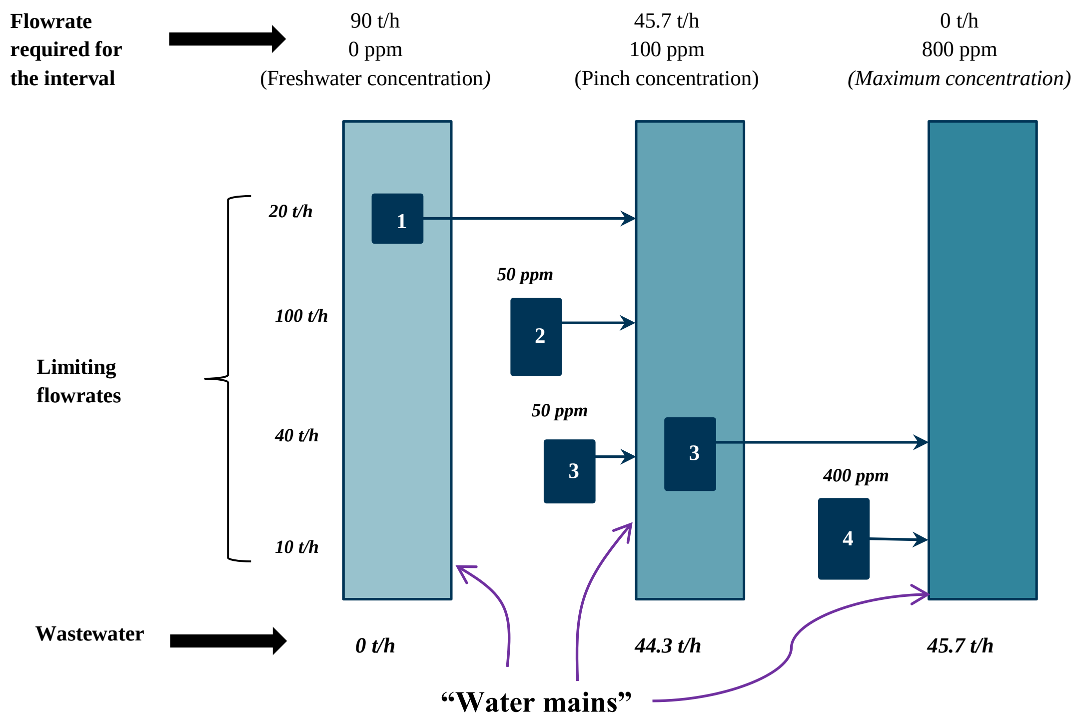


Figure 2.4.2 Water mains for the water network (Kuo & Smith, 1998)

The work of Dhole et al. (1996) was modified through the use of an evolutionary table to eliminate the problem encountered from mixing water sources (Sorin & Bedard, 1999). This was done by mixing source streams with closer concentration differences first, before progressing to the next nearest concentration. However, this numerical method proved to be unsuccessful for cases of multiple pinch points as it fails to identify the global pinch point, thus providing poor guidelines for process modifications and opportunities for recycling (Hallale, 2002).

As a result, Hallale (2002) improved on the above limitations by using a graphical method of water surplus diagrams (WSD) to account for the water composite curves. The construction procedure of the water surplus diagram is depicted in Figure 2.4.3. As observed in this diagram, the demand and source composites with their purity levels are plotted on the vertical axes while flowrates are plotted on the horizontal axes. The water surplus diagram is a plot of cumulative surplus against water purity, which is obtained after the identification of regions where the source composite is above the demand composite. The identified region implies surplus of pure water.

Some of the capabilities associated with the WSD technique include; the ability to deal with many water using operations, considers water losses within units and can account for operations with several inlets and outlet streams. One of the major contribution of the WSD technique include the establishment of the fact that the pinch point is found at one of the source concentration for fixed flowrate problems. Moreover, the technique highlighted the importance of the generation of the graphical plots of the water sinks/source graphs and the water surplus diagram, which gave rise to many pinch based techniques which will be brought into contention later in this work. However, the major disadvantage of the WSD is in its poor estimation of minimum water utility as long trial and error methods are used to obtain the water target (Mehrdadi, et al., 2009).

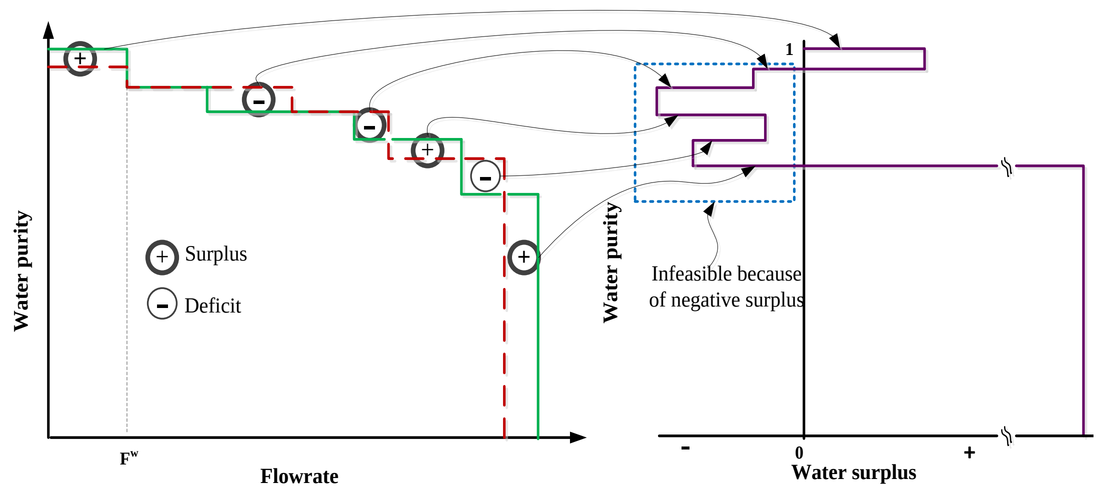


Figure 2.4.3 Construction procedure of the Water Surplus Diagram (Hallale, 2002).

In order to tackle the iterative nature of the WSD, Material Recovery Pinch Diagram was introduced by two groups of authors, El-Halwagi et al. (2003) and Prakash et al. (2005). In this technique, plots of sink and source composite curves are generated on a cumulative impurity load versus cumulative flowrate diagram. The pinch point is located by moving the source composite curve horizontally until it touches a single point on the sink composite curve. In the case of multiple freshwater sources, it is assumed that the secondary freshwater (with the lowest impurity amongst all sources) is essentially free (has zero cost) compared to the primary freshwater source. However, there are cases where purification costs are incurred for partial treatment of the secondary freshwater and such cases may require some optimization procedures to achieve optimal flowrates of both the freshwater sources (Foo, 2009). Although the technique successfully solved the direct reuse/recycle water network problem systematically in a single step, it has issues with visual resolutions of the graphical representations. This is apparent under cases where the slopes of the source and sink composite curves are closer or have similar values, thus making it impossible to locate the pinch point(s) without some magnification.

Tan (2002) proposed a water cascade table (WCT) method, which is also an improvement of the graphical WSD technique. The proposed technique attempts to eliminate the trial and error solution problem encountered in the work of Hallale (2002). This is a tubular-based numerical technique that is efficient for determining minimum water consumption and wastewater generation prior to network design. The technique has been successfully applied to water networks of single pure freshwater, impure freshwater source(s) and threshold problems of zero freshwater intake and zero discharge. The special feature of the technique is in its use and discarding of the interval freshwater flowrate column once the infeasibility (the occurrence of negative values in the cumulative load column) is removed from the network.

However, the zero freshwater intake threshold problems requires no interval freshwater adjustment while the zero discharge problems require some freshwater flowrate adjustment in order to generate positive wastewater flowrates. Foo et al. (2006) attempted to improve on the work by Tan (2002) by proposing a sequence of finally getting the right freshwater target. Nonethless, the WCT technique developed had difficulties in estimating the initial freshwater flowrate for cases where the overall water demand flowrate is equal or greater than the wastewater flowrate. Since the technique is purely algebraic, it limits designers from obtaining conceptual insights of the solved water network problem. Moreover, the technique had no guidelines for estimating the initial freshwater flowrate for multiple water sources or sinks and also failed to determine the minimum utility solution for instances where there is no negative value in the cumulative water surplus column (Mehrdadi, et al., 2009).

In addition, other algebraic targeting techniques include the Algebraic Targeting Approach proposed by Almutlaq et al. (2007) for impure freshwater usage through material recycle/reuse networks. This technique is based on the principles of Material Recovery Pinch Diagram. The technique was initially proposed for pure freshwater source by Almutlaq and El-Halwagi (2005). In the case of pure freshwater source, the source composite curve is horizontally moved to the right side such that the feasibility condition is not violated. This condition states that the flowrate of sources must be greater than or equal to that of sinks at any given load (Almutlaq & El-Halwagi, 2005).

As a result, the pinch point is located such that it corresponds to values in which the cumulative flows of the sources equate to those of the sinks while the cumulative loads of the sources equal to the maximum permissible loads by the sinks. The only adjustment made for the case of impure freshwater is that of the load contribution of the impure freshwater feed, which is simply the product of its flowrate and concentration. In this context, a shortcut technique is developed that eliminates the load from the impure freshwater source and thus transforming the flows, loads and residuals of the water network to take the same shape as in the case of pure freshwater targeting (Almutlaq, et al., 2007). All these efforts make the targeting procedure of the pure freshwater source also applicable for the impure freshwater source network.

Another attempt to improve on the WSD technique was embarked upon by Gomes et al. (2013), who extended the aforementioned technique by developing a procedure that identifies reference contaminant for multiple contaminants and processes in a water using network (WUN). However, the technique failed to provide essential and optimal guidelines in determining the reference contaminant and could not avoid concentration violations in unit operations, thus leading to unnecessary efforts to the construction of the WSD (Francisco, et al., 2015). Furthermore, the aforementioned modifications in the WSD technique were limited to operations with fixed contaminant load (FL). The detailed approaches for solving the water network problem with multiple contaminants will be discussed in subsequent sections herein

ii) Regeneration targeting techniques

Regeneration targeting techniques involving graphical insights have been developed over the years to solve the water network problem. Regeneration refers to the partial or total treatment of the wastewater before it is reused in other processes or recycled to original processes (Foo, 2009). The earlier work in this field is that of Smith and his colleagues (Wang & Smith, 1994); (Kuo & Smith, 1998). These authors based their regeneration targeting technique on limiting composite curve. The authors found that larger reduction in freshwater requirements are obtained in the case of regeneration recycle than re-use for obvious reasons associated with water savings in the former case. These deductions are depicted in Figure 2.4.4, where steeper slopes are for regeneration recycle. However, the main assumption and also the greatest limitation of this technique is that, the optimal inlet concentration for regeneration is equal to the pinch concentration, $C_{PINCH} = C_{Rin}$. This pinch is the point of interception between the limiting composite curve and the water supply line without regeneration. However, pinch reallocation sometimes occurs after regeneration is incorporated in the water network, thus making the assumption of $C_{PINCH} = C_{Rin}$, invalid and consequently failing to achieve minimum water targets (Mann & Liu, 1999).

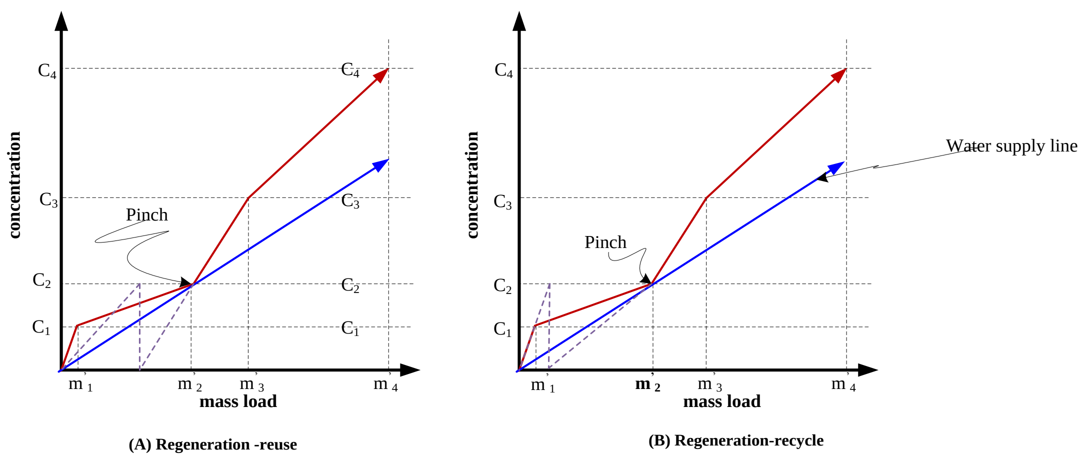


Figure 2.4.4 Targeting using the limiting composite curve for fixed load problem (Wang & Smith, 1994).

As a result, researchers such as Bai et al. (2007), in addition to locating minimum regeneration flowrate, attempted to solve the pinch reallocation problem by allowing for higher regenerator inlet concentration [$C_{Rin} > C_{PINCH}$], illustrated in Figure 2.4.5. This helps to account for cases where the limiting composite curve has more than one turning point near the water supply line (hence more optimum inlet concentration for regeneration), thus resulting in multiple pinch points. In their work, they proved with the construction of a composite WSL that by allowing the direct reuse/recycle pinch concentration to be the inlet concentration for regeneration leads to suboptimal regenerated water flowrate.

This is because there is an observed migration of the original pinch to a lower concentration and this implies that the water-using processes in the systems will receive poor quality water unless more freshwater is used in the system. Bai et al. (2007) also proved in their work that partial regeneration water networks are identical to regeneration recycling systems in terms of their graphical representations. Their difference is in quantitative analysis of their relationship between freshwater flowrate and regenerated water flowrate. There is a higher or equal amount of regenerated flowrate compared to freshwater for regeneration recycling systems while the regenerated water flowrate is smaller than that of freshwater for partial regeneration systems (Bai, et al., 2007).

On the other hand, water networks of total regeneration have the same amount of regenerated water as freshwater flowrate under cases where there are no water losses or gains in the system. Although the authors investigated the effect of varying the inlet and outlet concentration on the regenerated water flowrate, their technique entirely relied on fixed post regeneration concentration and this limits accuracy in the results.

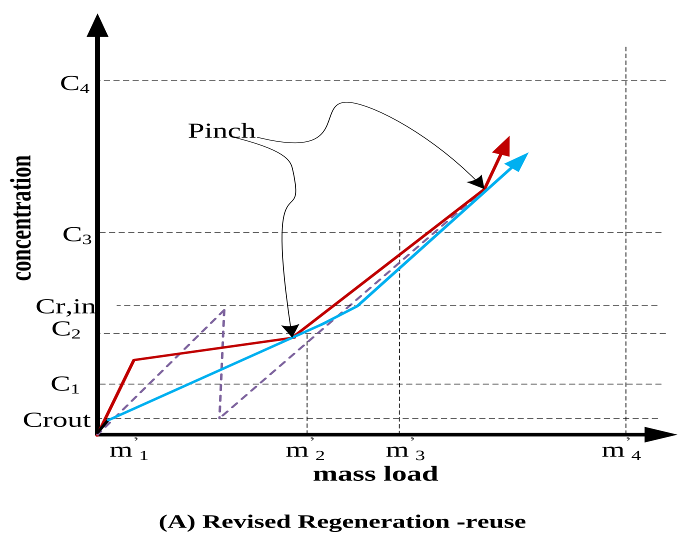


Figure 2.4.5 Revised targeting technique for regeneration- reuse using limiting composite curve (Bai, et al., 2007).

There are several researchers who explored the regeneration targeting problem focusing on water networks of fixed flowrate problem. This includes the work of Hallale (2002), who investigated the best region to place the regeneration unit in the water network using the water surplus diagram (WSD). The choice was made amongst locating the regenerator below, across or above the pinch concentration. It was found that the regeneration unit is best located above or across the pinch concentration to minimize both freshwater requirement and wastewater production as water can be transferred from the surplus region (which is below the pinch concentration) to the region above the pinch point, that which is deficient in clean water (Hallale, 2002).

Other authors such as Manan et al. (2004) followed the same guidelines of the WSD above but instead applied them on an algebraic targeting technique of Water Cascade Analysis. However, these techniques suffers from optimality issues due to their inability to guarantee minimum targets for the regenerated water flowrate along with both freshwater and wastewater flowrates.

On the other hand, Ultimate Flowrate Targeting proposed by Ng et al. (2007) is one of the few techniques that attempts to determine the minimum regenerated water flowrate along with minimum targets of freshwater and wastewater flowrate. The algorithm developed for the Ultimate Flowrate Targeting technique is summarized in Figure 2.4.6 below. In summary, the technique initially divides the sources and sinks within the water network into two sub-regions, namely; the freshwater region (FWR) and the regenerated water region (RWR) (Ng, et al., 2007). In the freshwater region, water sinks are supplied by freshwater, regenerated water and sources with concentration lower than the regenerator outlet concentration. On the other hand, sinks in the regenerated water region are supplied by regenerated water and sources in that region, which has concentration higher than regenerator outlet concentration.

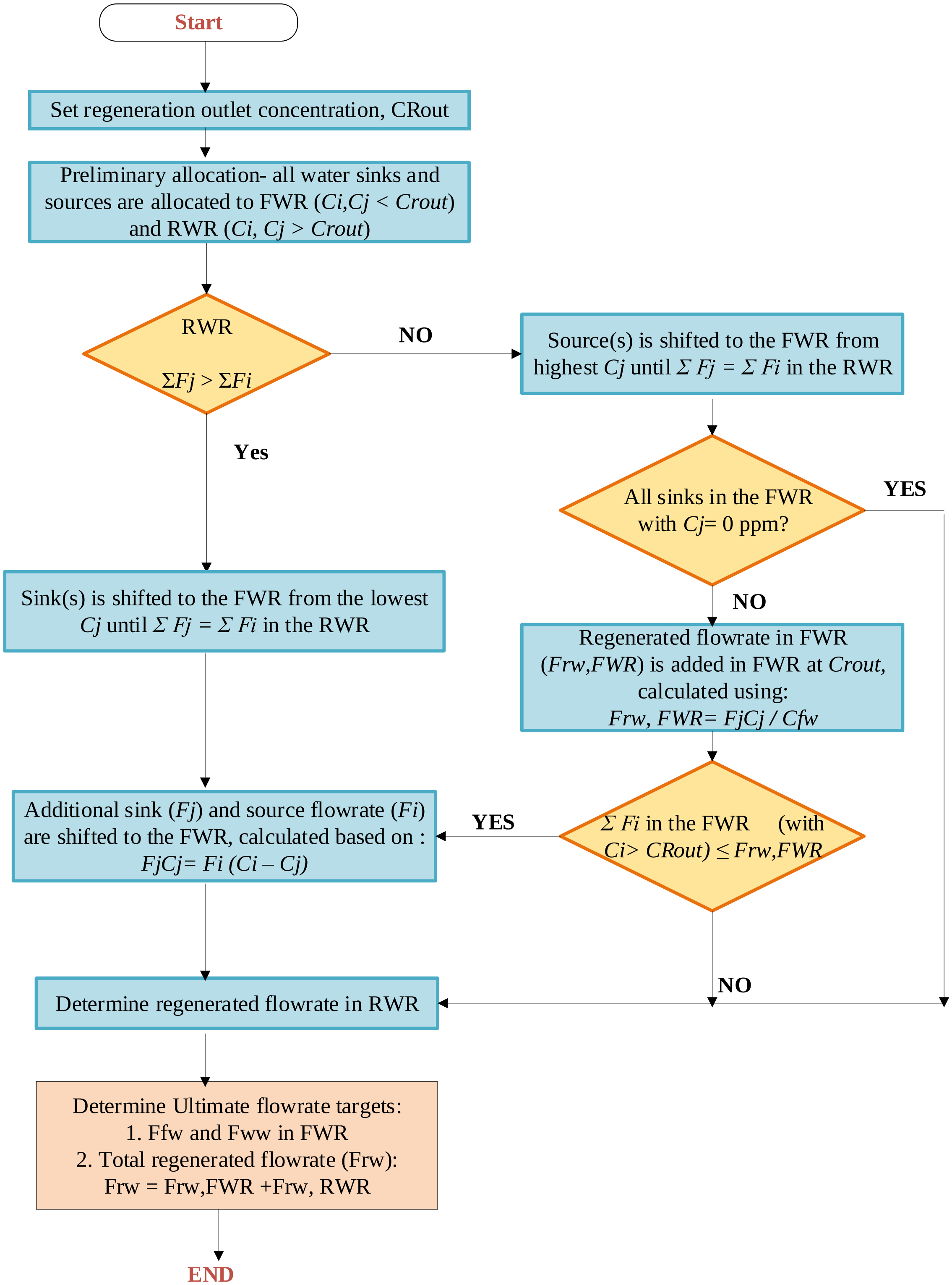


Figure 2.4.6 Ultimate flowrate targeting algorithm (Ng, et al., 2007)

According to Ng et al. (2007), ultimate flowrate targets are found after reallocating excess sources from the RWR to the FWR and then targeting for minimum flows of freshwater, wastewater and regenerated water in the individual regions using Water Cascade Analysis (WCA) technique. The proposed technique however does not cater for special cases where the total source flowrate is lower than the targeted regenerated flowrate in the fresh water region. As a result, later work by Ng et al. (2008) revised the targeting technique by reallocating additional sinks and sources in the RWR to the FWR so that the sinks in the FWR receive feed water at its highest allowable concentration and thus minimizing the regenerated water flowrate in the RWR.

Although the Ultimate Flowrate Targeting technique successfully determines regenerated water flowrate simultaneously with minimum freshwater and wastewater targets, it is limited to regenerators of fixed outlet concentration and therefore cannot be applicable to removal ratio (RR) type regenerators. In order to overcome this limitation, a source composite curve was proposed by Bandyopadhyay & Cormos (2008). The detailed description of the source composite technique shall be discussed in the section of targeting techniques for the total water network.

iii) Targeting techniques for wastewater treatment

Stringent environmental regulations on effluent discharge have enforced the need for wastewater management in industries. However, installation of wastewater treatment units is capital intensive, but this cost can be reduced through minimization of the effluent flowrate in the water network. As a result, much effort in literature has been directed towards developing techniques which can target optimum wastewater flowrates prior the design of the appropriate wastewater treatment system. The type of effluent treatment process is dependent on the type and concentration level of contaminant present in the wastewater stream. This means that a highly concentrated waste stream requires intense treatment systems in order to meet environmental discharge limits.

Several techniques have been developed over the years to target minimum effluent flowrate in order to meet environmental regulations. The treatment systems characterized by either fixed outlet concentration (C_{out}) and fixed removal ratio have been used in literature to solve both fixed load and fixed flowrate problems. This arises when regenerator is assumed to be a “black box”, with no detailed design. Wang and Smith (1994) developed and approach for the design of distributed effluent treatment systems for fixed load problems. In this approach, an impurity versus load diagram was constructed to locate the minimum treatment flowrate through drawing a treatment line from C_{out} to the point it touches the wastewater composite curve (Wang & Smith, 1994). However the technique is limited to a single treatment unit, in response, Kuo and Smith (1997) extended the aforementioned procedure for multiple treatment processes.

In the case of treatment targeting techniques for fixed flowrate problems, researchers such as Ng et al. (2007), developed a targeting technique for minimum treatment flowrate and minimum number of treatment units for both treatment systems of fixed outlet concentration and removal ratio type. A plot of impurity load versus flowrate is used to locate these targets on a wastewater composite curve. The technique is based on principles of material recovery pinch diagram. The targeting technique first involves the identification of the wastewater streams using either a graphical approach of material recovery pinch diagram or an algebraic approach of water cascade analysis (Foo, 2009).

Then the identified wastewater streams are arranged in an increasing order of impurity concentration to construct the wastewater composite curve as illustrated in Figure 2.4.7. In order to obtain the maximum allowable impurity load that can be discharged to the environment, a discharge locus is added on the plot of impurity load versus flowrate diagram. The height of the discharge locus provides the maximum impurity load (Δm_D) for discharge. Then the total impurity load (Δm_T) that can be removed from the wastewater streams before discharge is given as the difference between the wastewater composite curve and the waste discharge locus. Moreover, the load to be removed by the treatment unit is given as Δm_R and F_T is the minimum treatment flowrate for the overall network.

Although the technique successfully locates minimum treatment flowrates for both treatment units of fixed outlet concentration and fixed removal ratio, there are no guidelines on how it can be adapted to obtaining targets for the same treatment units in multiple numbers. Moreover, there is no evidence that the approach can be extended to target minimum treatment flowrate for fixed inlet concentration to the treatment units.

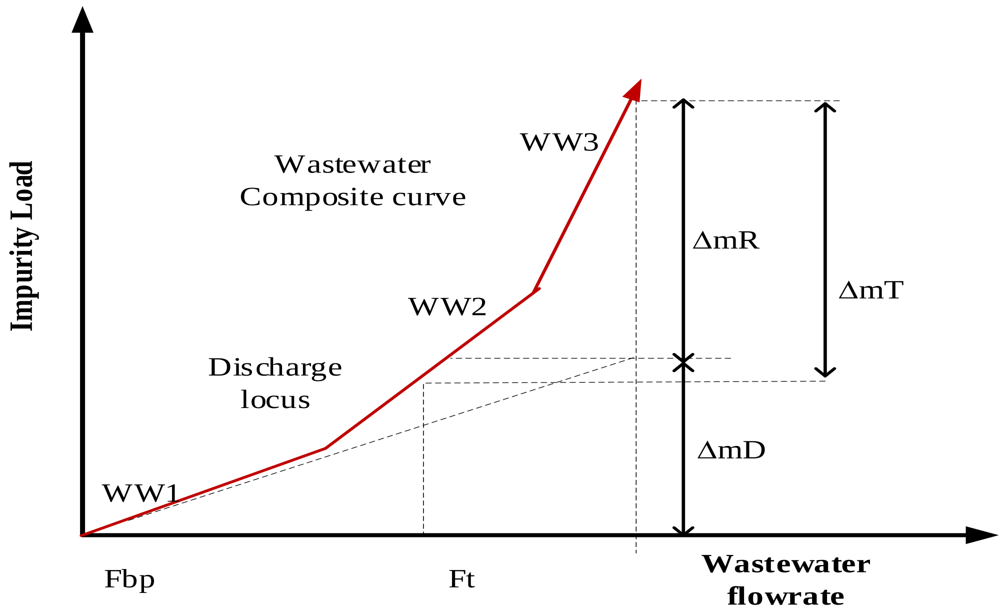


Figure 2.4.7 Targeting for the distributed waste treatment (Ng, et al., 2007)

iv) Graphical targeting techniques for the total water network

The above discussed graphical targeting techniques are for fixed load problems and either limited to regeneration targeting or water re-use/recycle targeting. However, targeting for the total water network has advantages such as simultaneous minimization of freshwater, regenerated water and wastewater production. Moreover, both flowrate and consequently cost optimization can be conducted upon the overall water network without compromising certain sections of the network. As a result, the individual sections of water reuse/recycle, regeneration reuse/recycle and wastewater treatment can be integrated to yield optimal targets at acceptable environmental discharge limits. The interactions between the different systems are depicted in Figure 2.4.8 below.

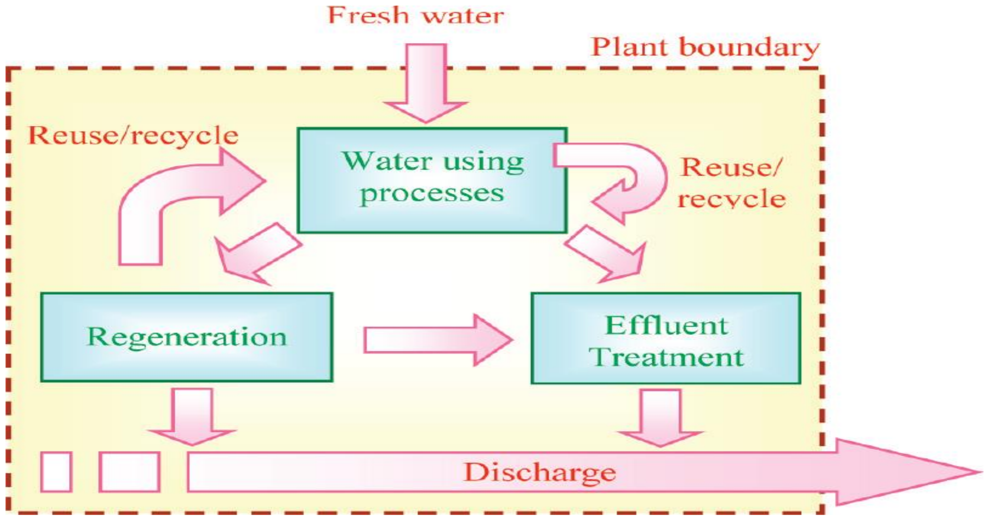


Figure 2.4.8 The overall framework of the total water network (Kuo & Smith, 1998)

Kuo and Smith (1998) are the earliest researchers who attempted to target for a total water network for fixed load problems. However, the technique developed by these researchers failed to provide proper guidelines to ensure optimum water network with minimum flowrates and impurity load removal for the overall network. On the other hand, several authors as discussed below proposed techniques to solve the fixed flowrate problem of the water network.

In order to solve the total network for the fixed flowrate problem, Ng et al. (2007) proposed a sequential targeting technique for the individual elements of water reuse/recycle, wastewater stream identification and regeneration reuse/recycle. The objective was to determine minimum targets in each section before proceeding to the next stage. In this way, the subsequent stages will have some initial or starting point prior their targeting procedure. This is particularly clear in the case of the wastewater streams, which are first identified and then summed up to locate the inlet flowrate to the regenerator. However, the sequential nature of the technique limits accuracy in the targeted flows. This is because upon optimizing the overall network, the targeted flows of the individual sections are likely to change. Additionally, the technique cannot cater for regenerators with outlet concentrations higher than the environmental discharge limit and there is no evidence of minimum flow targets obtainable for multiple regenerators' network.

Another attempt to target for the total water network was conducted by Bandyopadhyay & Cormos (2008). The authors proposed a Source Composite Curve, which is a plot of the maximum contaminant load at different contaminant concentrations. The representation of the technique can is illustrated in Figure 2.4.9, where different regenerators of fixed removal ratio and fixed outlet concentration are explored. The targeting technique is carried out only in a single stage and this makes the procedure attractive over other sequential targeting techniques. The regenerator used in this technique is multipurpose as it can perform both regeneration reuse/recycle and serve as a wastewater treatment facility where all necessary contaminant loads can be removed to meet environmental discharge limit. Although its simplicity and versatility makes it advantageous over other total water network targeting techniques, it is restricted to single regenerator water network. This limitation allows for no exploration of further freshwater savings through multiple regenerators of different performance indices.

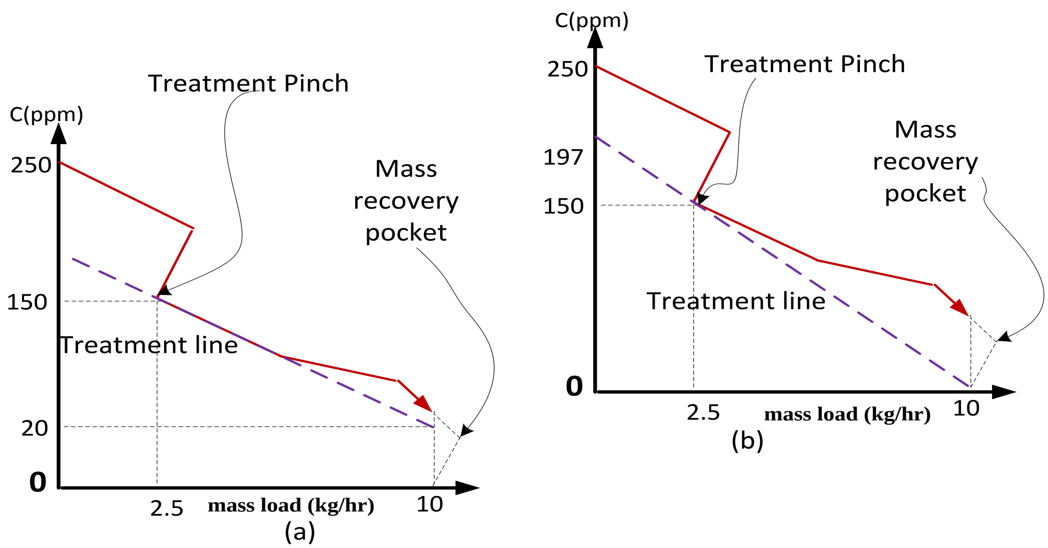


Figure 2.4.9 Source composite curve: (a) treatment unit with fixed outlet concentration, C_{out}=20 ppm; (b) treatment unit with fixed removal ratio RR=0.95 (Bandyopadhyay & Cormos, 2008).

Moreover, other techniques which solved the total water network synthesis include the Improved Problem Table (IPT) by Deng et al. (2016) and the Automated Composite Table Algorithm (ACTA) by Parand et al. (2016). These techniques used the principles of Composite Table Algorithm (CTA) by Agrawal & Shenoy (2006) to achieve minimum targets of freshwater and wastewater generation. The distinct features of the CTA technique are that it is non-iterative; it can handle operations with water losses/ gains and those with multiple inlet or outlet streams (Agrawal & Shenoy, 2006). Moreover, it can solve water networks of both fixed flowrate and fixed load problems. However, in the case of fixed flowrate problems, the procedure requires the conversion of the data to a fixed load type in order to accommodate the subsequent generation of a limiting composite curve (LCC), which is carried out on the basis of a fixed mass load. This approach allows for the achievement of minimum freshwater and wastewater targets, which can be derived from the interception of the plots of LCC and the water supply line (WSL). The major assumption applied to carry out this conversion is that; initially the sinks or demands are allowed to receive an infinite amount of load. This assumption is relaxed when sources are introduced in the system to generate a Limiting Composite Curve (Agrawal & Shenoy, 2006). The procedure is illustrated in Figure 2.4.10 (a) below, where all demands has an initial mass load of zero, which increases until an arbitrary concentration of 300 ppm. The plots of D1 to D4 are generated from provided information about flowrates and inlet concentrations of each sink while the demand composite curve is obtained from the summation of mass load within each concentration interval.

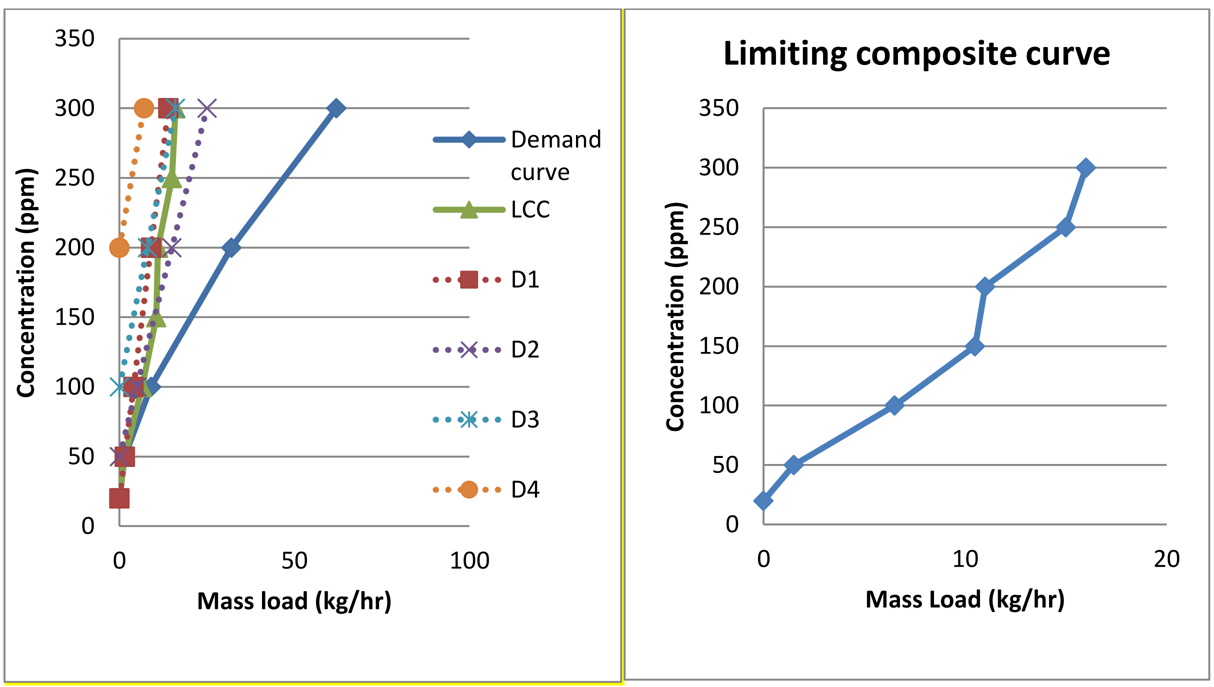


Figure 2.4.10 (a) Individual demand profiles and demand composite curve (Agrawal & Shenoy, 2006) b) Limiting composite curve

In reference to Figure 2.4.10 above, the introduction of the sources into the demand composite curve is conducted at the concentration at which they are initially provided in the system (Agrawal & Shenoy, 2006). The procedure involves the subtraction of the source flowrate from the sink composite curve. The resultant limiting composite curve has lower flowrates and consequently increased slope segments as seen in Figure 2.4.10 (b).

Also using the principles of CTA, Deng et al. (2016) modified the Improved Problem Table for a flowrate targeting problem with multiple partitioning interception units. The interception units or rather regenerators are characterized by both fixed removal ratio and specified liquid recovery. The authors successfully solved the total water network for both the fixed flowrate problem and the fixed load problem. In their procedure, the Excel Goal Seek feature was used to obtain optimal solutions. The results obtained were validated with an automated targeting model developed by Ng et al. (2009). Another technique developed in this context is the ACTA by Parand et al. (2016). In this work, the CTA was automated to explore the interactions between key parameters such as pre-regeneration concentration and post-regeneration concentrations and their effect on the overall water network. The authors successfully determined the optimum regenerator performance (the post regenerator concentration, Co) prior the water network design using cost functions. Their technique is however limited to a single contaminant water network consisting of a single pass regenerator. This type of regenerator is assumed to have negligible flow losses and this is generally impractical for industrial applications.

v) Targeting techniques for multiple contaminant water network

Although pinch based techniques are attractive for their simplicity and provision of conceptual insights, they are inherently limited to single contaminant systems (Khor, et al., 2011). There are few techniques within the area of pinch analysis, which attempt to solve for the multiple contaminant problems. This includes the work of Calixto et al. (2015), who proposed a novel algorithm to determine both the reference contaminant and operation. This algorithm is an improvement of the work done by Gomes et al. (2013). In addition, the authors proposed a novel algorithm to predict concentration violations in unit operations and this proved to be a major contribution to solving the WSD as upon identification, these violations can be removed. One other major advantage of using these techniques is that; freshwater targets and water network designs can be achieved for systems of either fixed load or fixed flowrate operations, for both single and multiple contaminant problems. The following is the criteria to properly select the reference contaminant and operation (Calixto, et al., 2015):

Table 2.4.1 Criteria for determining reference contaminant and operations

Reference Contaminant	Reference Operation
• **Must have the lowest maximum inlet concentration for all operations**	• Requires the cleanest external water source (essentially freshwater)
• **Must be monotonic (have its outlet concentration from an operation greater than the sum of concentrations from precursor processes)**	• An operation with the lowest inlet concentration
• **Must have the highest $G_{u,c}{}^{w}$ parameter (reach first its maximum inlet concentration when freshwater is used)**	• An operation with the lowest outlet concentration
• **Must have the highest $R_{u,c}$ value (relation for water savings in unit operation)**	

The algorithm for determining the reference contaminant is summarized in Figure 2.4.11 below. Note that the procedure proposed in the algorithm below is adopted in this work to solve the multiple contaminant water network and this shall be demonstrated in chapter 4 of the results.

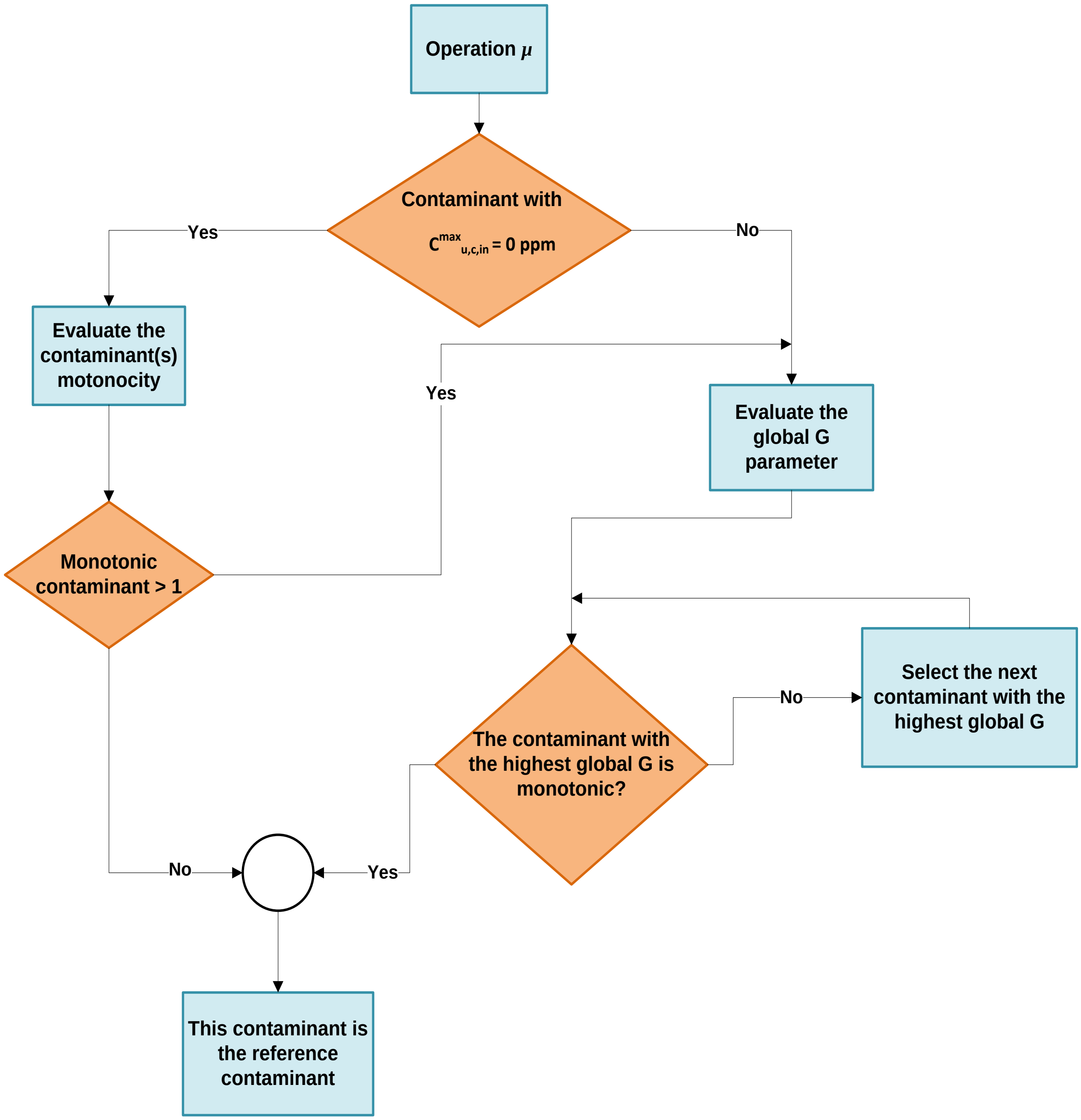


Figure 2.4.11 Algorithm for the selection of the reference contaminant (Calixto, et al., 2015)

In a broader view, pinch based techniques successfully minimizes targets for freshwater and wastewater. However, there are some limitations associated with the use of graphical methods for water network design and these are listed below:

- Graphical methods cannot handle multiple contaminant problems (Hallale, 2002).

- The technique is tedious and inaccurate in handling complex systems of multiple sources, treatment units and sinks (Kuo & Smith, 1997).

- The technique accounts only for concentration and flowrates constraints and excludes geographical, economic and safety constraints (Doyle & Smith, 1997).

Some of these limitations can be avoided through the use of mathematical models to design the water network. These mathematical techniques are discussed in the ensuing section.

2.4.2 Mathematical optimization

The earlier work in mathematical optimization approach to water network synthesis was conducted by Takama et al. (1980) . The authors proposed a superstructure-based non-linear optimization technique to address the problem of optimal water allocation in a petroleum refinery. The work aimed at integrating fixed load sinks (water using operations) and wastewater treatment units in order to explore opportunities of water re-use and regeneration for a single contaminant problem (Takama, et al., 1980). The model developed used NLP with nonconvex bilinearities and nonlinear cost based objective function, which was minimized with a penalty on discharge constraint (Khor, et al., 2014).

Later, Doyle & Smith (1997), modified the work of Takama (1980) by developing a sequential superstructure-based optimization approach, wherein, initialization of the NLP problem was performed using linear programming (LP) approximation technique. The technique was developed for multiple contaminants and sinks with fixed outlet concentration. However, the major drawback associated with this technique is that global optimal solution cannot be guaranteed.

In most work of researchers, the water network synthesis problem is solved using either a detailed regenerator or black-box type regenerators. It is noteworthy that techniques which incorporate detailed regenerator design within the water network can account for energy consumption of wastewater treatment and therefore minimize it. However, water networks embedded with black-box type regenerators are mainly focused on water minimization rather than energy.

In the case of the black box approach, other mathematical techniques for the water network synthesis include the work of Tan et al. (2009), who developed a non-linear formulation that integrates a single, centralized partitioning regenerator with a source-sink superstructure for a single contaminant problem. The authors used a branch and bound method to solve the resultant nonconvex NLP. The model formulation incorporated a single partitioning type regenerator within the water network and successfully minimized the freshwater requirement. However, the energy utilization part of the network did not form part of the objective function as energy can only be accounted for by a detailed regenerator representation. Moreover, the optimization technique does not include piping interconnections costs.

In addition, authors such as Galan and Grossmann (1998) solved the wastewater treatment network using sequential heuristic search procedures where McCormick's LP relaxations are used to solve the NLP and MINLP model formulation. In their work, the water network representation is of a fixed load type for a multiple contaminant system. The regenerators considered are black-box membranes which do not capture and minimize energy consumption within the water network due to their lack of detailed design. Despite the potential of the proposed technique, global optimal solutions cannot be guaranteed (Khor, et al., 2014).

In contrast, Meyer and Floudas (2006) instead, solved the fixed flowrate water network with a black-box regenerator of fixed removal ratio. The resultant model was a MINLP with nonconvex bilinearities. The proposed solution strategy involved the MILP based piecewise-affine relaxation based on reformulation linearization technique (RLT) (Meyer & Floudas, 2006). In this case, the bilinear terms are replaced with the new RLT variables in order to linearize the model. The idea was to use similar piecewise-affine relaxation method to carry out spatial branch and bound optimization with a tighter lower bound. Although the technique successfully achieve minimum freshwater and wastewater targets for the total water network designed, the requirement of additional 0-1 variables for the MILP model prompted the need for further reformulations which make the technique computationally intensive.

In the case of water networks with detailed regeneration design, true total network cost can be determined, that which takes into account both water and energy savings within the network. The research work which supports this approach includes the work of Khor et al. (2011), who improved the formulation by Tan et al. (2009). The improvement was achieved through incorporating multiple contaminants and including piping interconnection cost in the objective function. As a result, the proposed superstructure entails continuous variables for both the contaminants and flowrate, binary variables for the piping interconnections and the nonlinear detailed reverse osmosis network. The resultant model is a MINLP model formulation. In the work of Khor et al. (2011), the water network synthesis is carried out with a single regenerator of a fixed design. The implication of a fixed regenerator design is that prior to the design of the water network, there were already specifications in the number of regenerators required, the number of pumps and recovery turbines needed. However, the major limitation of such an approach is that there is limited flexibility in the model and that reduces solution optimality. Nevertheless, Khor et al. (2011) successfully minimized the objective function which now incorporates energy consumption and achieved minimum flow targets through exploiting the different opportunities of water reuse/recycle and regeneration reuse/recycle.

Additional research work which looked at detailed regenerator design for water network synthesis include the work of Yang et al. (2014), Buabeng-Baidoo & Majozi (2015) and Mafukidze &Majozi (2016). In the work of Yang et al. (2014), multiple wastewater treatment technologies were considered to determine the trade-off between the removal efficiency of the regenerator and the treatment cost. These technologies include; ultrafiltration (UF), reverse osmosis (RO), sedimentation, ion-exchange, activated sludge and trickling bed all of which were designed using short-cut models. Furthermore, the impact of removal ratio and the treatment cost on the water network were evaluated. However, the disadvantage of the work is that the short-cut models used do not provide true regeneration costs as they are not a reflection of the detailed design of the treatment units.

To accurately capture the true regeneration cost and achieve model flexibility, for example; in terms of the number of regenerators and pumps requirement, Buabeng-Baidoo & Majozi (2015) enhanced the work by El-Halwagi (1992) to incorporate the proposed reverse osmosis network (RON) within a water network superstructure. The authors successfully demonstrated the benefits of exploring multiple regenerators within the water network, allowing for the model to determine an optimal removal ratio (*RR*) and the impact of energy consumption on the overall objective function. It was observed that a variable RR impacts greatly on the cost and structure of the network while multiple regenerators reduce both freshwater requirement and wastewater generation (Buabeng-Baidoo & Majozi, 2015). However, the complexity of the proposed model results in large computational times. This is a challenge that can potentially be bridged through the development of effective mathematical modelling pre-processing techniques which are explored in this treatise. On the other hand, Mafukidze & Majozi (2016) looked at detailed multiple electrodialysis regenerators design within the water network instead of RON. Their work is however limited to a single, ionic contaminant and it is therefore not a true reflection of industrial wastewater.

2.4.3 Integrated water and membrane water networks using a hybrid framework

i) Membrane systems for water treatment network

Wastewater treatment systems can be non-membrane types (such as distillation, absorbers and strippers) or membrane types such as reverse osmosis, forward osmosis, ultrafiltration, microfiltration, nanofiltration, electrodialysis, electrodeionisation and membrane distillation (Wang, et al., 2011). The choice of the appropriate membrane system is dependent on the type of contaminant, contaminant concentration level and the operation requirements of subsequent processes which the regenerated water is to be used. In accordance to Judd et al. (2003), increasing popularity of membrane systems in wastewater management is due reasons such as; high selectivity, use no expensive chemical additives, high energy savings and effective separations at room temperature. The following is the classification of these membranes based on their different driving forces:

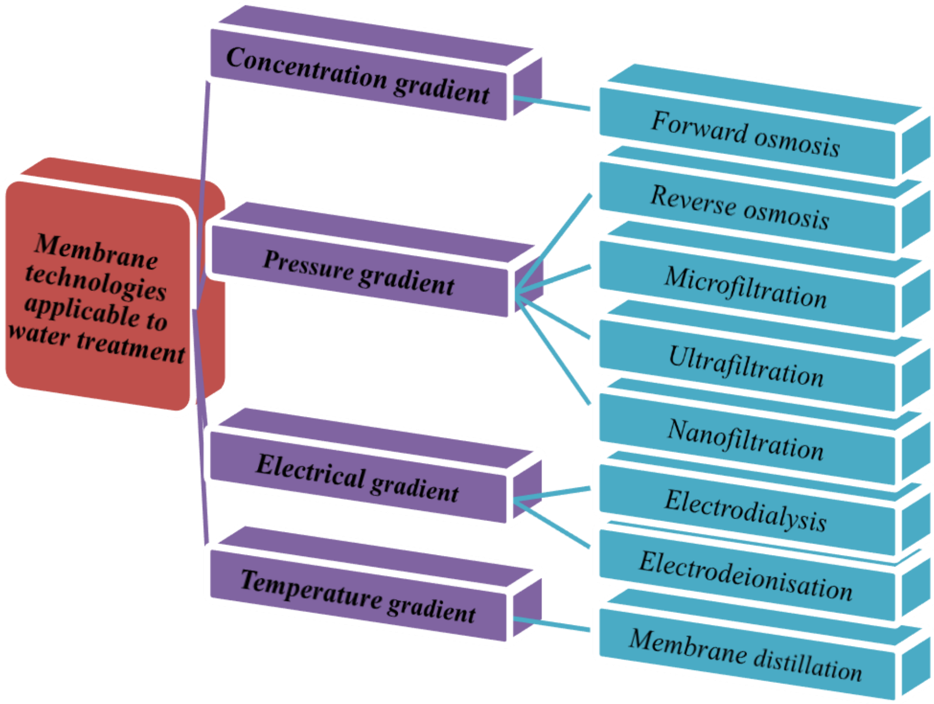


Figure 2.4.12 Classification of membrane technologies according to their different driving forces (Judd & Jefferson, 2003).

The principles of operations for these driving forces are described as follows (Wang, et al., 2011):

- **Pressure-driven**: Speed of species separation based on their sizes is enhanced through the application of Hydraulic pressure.
- **Electrical potential-driven**: Separation of charged and uncharged species is carried out through the application of electrical potential.
- **Concentration-driven separation**: This separation is achieved by virtue of the species' different diffusion rates.
- **Temperature-driven separation**: Temperature difference across the membrane gives rise to vapour pressure gradient which initiate this separation.

As illustrated in Figure 2.4.12, Forward Osmosis membrane (FO) is a concentration driven type membrane. These membranes use osmotic pressure gradient for their separation, wherein a semipermeable membrane is used as a separation unit to move water molecules from a low contaminant concentrated solution to a solution of high contaminant concentration until equilibrium. FO membranes are mostly used to pre-treat RO membranes (Lee, 1981). On the other hand, reverse osmosis membranes (RO) are pressure driven separation technologies. The principle of operation for RO membranes is the opposite of FO membranes as hydraulic pressure is applied in RO membranes to overcome osmotic pressure and consequently result in the movement of solvent molecules from a concentrated solution to the less concentrated solution. The separation in RO membranes results into two streams of permeate (with low contaminant concentration) and retentate (with high contaminant concentration). RO membranes have successfully applied in the desalination of seawater and brackish water (Maskan, et al., 2000) and the removal of small organic molecules and dissolved ions (Saif, et al., 2008a).

Other pressure driven membranes are Ultrafiltration (UF), Nanofiltration (NF) and Microfiltration (MF) membranes. In MF membranes, the separation process is such that a solution is allowed to flow perpendicularly to the porous membrane. The pore size range is of 0.1µm to 10µm (Baker, 2012) and the separation is carried out at low pressures of 0.2 bar to 5 bar. This technology is used in the dairy sector, pharmaceuticals and clarification processes of alcohol or juice, water treatment and etc (Baker, 2012). These membranes also operate on low pressures ranging from 0.2 bar to 5 bar (Perry & Green, 2007). Moreover, there are UF membranes, in which a molecular weight cut-off (MWCO) is used to characterise the membrane. MWCO refers to the 90% weight of the solute that is retained on the membrane and therefore only 10% of the solute passes through it. UF membranes have pore sizes of 0.001-0.01µm, which is smaller than that of MF. According to the Water Environment Federation (2006), these membranes can purify contaminated solutions of particulates, bacteria, colloids, macromolecules, suspended solids and dispersed fluids.

The other membrane technology that is pressure driven is Nanofiltration (NF) membrane. This membrane uses high pressure to remove mainly large ions and has pore size range of 0.0001-0.001µm. These pores are very small and that feature makes it difficult and costly for the NF membranes to be used for industrial applications, wherein waste of large particle sizes need to be removed from the contaminated water. Unlike RO membranes, NF membranes have a lower rejection to monovalent ions. As a result, the most suitable applications of NF membranes are de-salting of process streams, removal of pesticides and etc. (Baker & Martin, 2007).

Furthermore, there are membrane distillation units which are temperature driven technologies in which a hydrophobic membrane is used to separate two phases on the basis of partial vapour pressure. During the process, the two distinct phases separated by a barrier generated by the membrane are the liquid phase and vapour phase from which the latter is allowed to pass through the pores of the membrane. There are some membranes which use electrical gradient for their separation and this includes electrodialysis and electrodeionisation. Electrodialysis separation is driven by direct electric current which initiates the migration of ions across both a cationic and an anionic exchange permselective membrane (Tsiakis & Papageorgiou, 2005). The application of ED is commonly for seawater desalination. On the other hand, electrodeionisation membrane is similar to an ED membrane. However, the difference lies in the additional ion exchange resins on the membrane units which are found in electrodeionisation. As a result of this addition, electrodeionisation membranes tend to have a longer life span than ED in the desalination o dilute solutions (Strathmann, 2004a).

Any of the above discussed membrane technologies can be used to address the water network problem. However, the focus will be on reverse osmosis for the purpose of this work. Important consideration is in the detailed design of the regeneration unit using mathematical optimization tools will be placed on obtaining the optimum membrane configuration. Therefore, for the case of reverse osmosis, design specifications to be considered are; number of elements per vessel, multi stage & passes, booster pumps, permeate blending & throttling and concentrate recycle. The detailed mathematical equations for the design of reverse osmosis are provided in chapter 3 of methodology. The following section provides background on RO membranes and the associated design principles.

a) Background on RO membrane

As described above, RO membranes are pressure driven processes in which a cross flow configuration is applied for wastewater separation. During this process, the contaminated water or the feed water stream flows tangentially to the membrane surface while a fraction of the feed passes through the membrane as the permeate. The remaining water, that which is rejected by the porous membrane, travels along the membrane surface and is termed the retentate. The distinction between the permeate and the retentate streams is that, the former contains almost pure water with low concentration of ions and the latter contains high concentration of small particles and dissolved ions. The configuration of these flow patterns is illustrated in Figure 2.4.13 below, with the membrane surface depicted by the red dotted line.

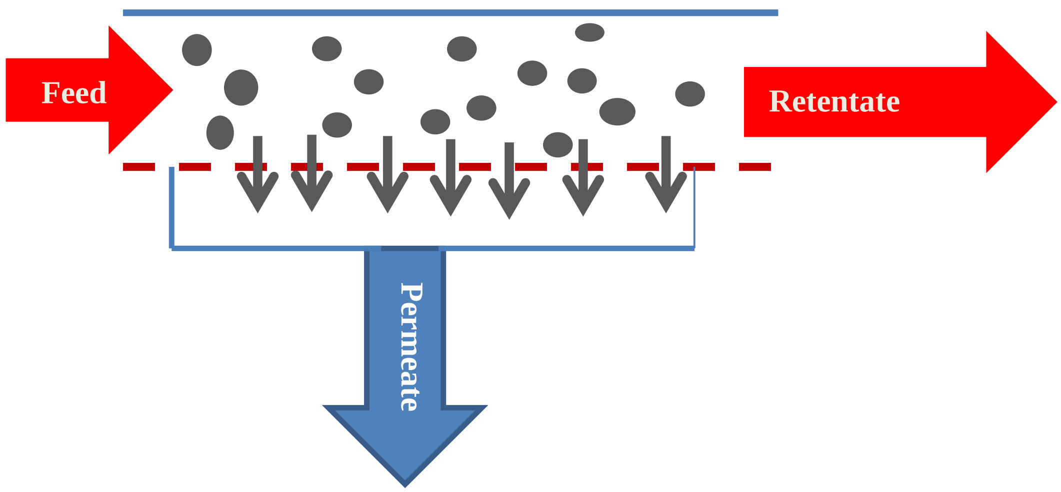


Figure 2.4.13 Schematic flow of RO membrane

The separation in reverse osmosis membrane is based on the concept of chemical potential difference. This potential difference results from the difference in solute concentrations within the feed water stream when exposed to a semi-permeable membrane. In this situation, the chemical potential difference results in an osmotic flow, wherein the contaminated solvent travels across the membrane and transfer pure water through the semi-permeable membrane from a low to high concentration solution (Saif, et al., 2008a). This movement of water occurs until the chemical potential is equal on both sides of the membrane and that is termed osmotic equilibrium. In other terms, the process continues until the pressure difference across the membrane is balanced.

b) Principle and design of RO membrane

In principle, reverse osmosis process involves the application of an external pressure, that which is greater than the osmotic pressure, to the concentrated solution. This is done with the purpose of reversing the natural osmosis phenomenon. During this process, the external pressure forces water to flow from the concentrated side to the dilute side while the membrane retains the solutes on it (El-Halwagi, 1997). The stream that carries the solutes with it is the retentate stream. There are four modules that can be used to distinguish the different configurations of RO units. These modules are plate and frame, hollow fibre, spiral and tubular wound (Evangelista, 1985).

Amongst the aforementioned modules, hollow fibre and spiral wound modules are popularly used for industrial applications due to their large surface area to volume ratio, negligible concentration polarization and the self-support strength obtained from their fibres (El-Halwagi, 1997). It can therefore be deduced that the appropriate module configuration is selected based on cost effectiveness in terms of manufacturing, operation and maintenance. Moreover, it is important that the selected configuration has higher performance (e.g. energy efficient) and minimal failures in terms of fouling and concentration polarization issues.

Following up on the above advantages, a hollow fibre membrane is selected in this work and the modelling part of it is dependent on both membrane transport equations and the hydrodynamic modelling approach.

According to El-Halwagi (1997), process activities on the membrane surface can be described by membrane transport equations while the hydrodynamic model describes the momentum, energy and the macroscopic transport of the different species. In the hydrodynamic model, pressure variation is described either as a constant pressure on the shell side or pressure difference across the fibres of the membrane. The pressure difference is induced by the pressure drop along the membrane fibre length and this also affects the permeate flowrate per HFRO module. This behavior can be illustrated with equation 2.1 below, adapted from the work of Khor (2011):

$$q_p(co) = S_m A\left\{P_F - \left(\frac{\Delta P_{shell}}{2} + P_p\right) - \frac{\pi_F}{2}\left(1 + \frac{C_{rej}(int,co)}{C_F(int,co)}\right)\right\}\gamma \qquad 2.1$$

Where γ is a dimensionless constant which is described by equation 2.2 below:

$$\gamma = \frac{\eta}{1 + \frac{16A\mu r_O L L_S \eta}{1.0133\times10^5 r_i^4}} \qquad 2.2$$

Also, S_m refers to the membrane area per module while P_F and P_p refers to the membrane feed and permeate pressure, respectively.

Furthermore, it can be determined from equation 2.1 above that the higher the pressure drop (ΔP_{shell}), the lower the permeate flowrate per HFRO module (q_p). The observed relationship between pressure drop and flowrate highlights the importance of capturing the correct axial and radial flows within the HFRO module. As a result, there are two transport equations used in literature to describe both the water and solute flux within the HFRO module. The constraint for the solute flux is described in equation 2.3 below:

$$N_{solute} = \left(\frac{D_{2M}}{K\delta}\right) C_S \qquad 2.3$$

Where $\frac{D_{2M}}{K\delta}$ is the solute flux constant through the HFRO membrane and C_S is the contaminant concentration in the shell side of the membrane. Moreover, C_S is described in constraint 2.4 as the average concentration between the reject and feed concentrations.

$$C_S = \frac{C_F + C_{rej}}{2} \qquad 2.4$$

Additionally, the constraint for the water flux is described in equation 2.5 below:

$$N_{water} = A\left(\Delta P - \frac{\pi_f}{C_f} C_S\right)\gamma \qquad 2.5$$

Where N_{water} describes the water flux, ΔP is the pressure difference across the membrane, π_f is the osmotic feed pressure while C_f and C_S refer to the feed solute concentration and the average solute concentration in the shell side, respectively.

Furthermore, the performance of a reverse osmosis membrane can be graded in reference to a few parameters and these include permeate flux, flowrate, salt rejection, pressure drop, transmembrane pressure and recovery rate (Abbas, 2007). In brief, some of these parameters such as salt rejection can be defined as the percentage of the amount of solute retained by the RO membrane. Then the recovery refers to that fraction of the feed flow which passes through the membrane and is therefore recovered in the permeate stream. Moreover, the flowrate provides information about the rate of flows for the feed, permeate and the retentate stream. These rates are used to grade the performance of a RO unit; meaning that e.g. a higher flowrate of the permeate stream is associated with higher liquid recovery and therefore a greater membrane performance. In addition, there is also a permeate flux that describes the quantity of permeate produced per both unit of time and RO membrane area.

c) Limitations of RO membrane

The performance of an RO membrane can be greatly affected by both concentration polarization and fouling. Concentration polarization in membrane separation occurs when there is accumulation of solute near the membrane surface and this adversely affects the solvent and solute recovery (Maphutha, et al., 2013; Kaushik, 2008). This is because the higher the concentration at the membrane surface, the lower the solvent and solute fluxes through the membrane (Evangelista, 1985). As a result, the consequence of concentration polarization, which also implies a lower concentration flowrate, is an increase in osmotic pressure.

In the case of fouling limitations, there can be a decline in the permeate flux, decreased product quality and increased feed pressure which consequently increases the energy consumption rate (Sassi & Mujtaba, 2011). Membrane fouling can be caused by suspended solids (e.g. iron, silica, inorganic or biological compound), scaling or the presence of colloids in the wastewater. As a result, membrane systems require regular maintenance to mitigate some of these fouling issues. According to Zhu et al. (1997), chemical pre-treatment of reverse osmosis can help increase the life span of these membranes. Other measures that can be taken to reduce fouling include keeping high cross-flow velocity on the feed side and operating at high temperatures (Lee & Frankiewicz, 2005). It can be noted that with high temperatures, permeate flux increases as a result of reduced water viscosity. This also results in an increase in solute permeation and thereby reducing fouling effects. However, the water network synthesis in this work entails wastewater flows of relatively low temperatures; hence the water network is assumed isothermal. As a result, chemical pretreatment is the main approach adopted in this work to mitigate fouling issues and reduce concentration polarization.

ii) Integrated graphical and mathematical modelling techniques for water networks

Although there are irrefutable merits in integrating mathematical techniques with graphical targeting techniques, there are few researchers who explored the integration of these techniques. Some advantages obtainable from the integration include benefiting from both conceptual insights and rigorous designs from mathematical modelling to produce optimal results. Most hybrid models, those which integrate physical insights with mathematical modelling are predominantly mathematical and only a few apply insight based concepts (Pinch based techniques) into mathematical programming. All these different approaches are discussed below.

The hybrid models which are predominantly mathematical include the work of Dhole et al. (1996) and Doyle and Smith (1997) . In particular, the approach developed by Dhole and co-workers involved application of mathematical programming in designing a water network of fixed flowrate framework. Subsequently, graphical representations of demand and source composite curves were generated from the mathematical programming results. These curves are plotted on a concentration versus load diagram, wherein it is assumed that both the sources and sinks have fixed concentrations and an aqueous stream of wastewater passes through all operations. Following the pinch principles, the point of interception of the two curves provides information about opportunities for water reuse and the minimum freshwater intake and the wastewater that can be generated by the network.

The challenge with the proposed technique is that there are no guidelines for eliminating multiple pinch points and therefore optimality of results cannot be guaranteed in cases where different sources are mixed to increase the amount of water reuse (El-Halwagi, et al., 2003). As a result, to improve on the aforementioned limitation, El-Halwagi et al. (2003) developed a technique that was fist formulated using mathematical modelling and converted it into graphical representations. The distinct feature of their technique is that optimality conditions derived from dynamic programming and parametric optimization are applied in the mathematical formulation to provide reliable targets for minimum water resources.

Furthermore, Doyle and Smith (1997) used a linear model to initialize a nonlinear optimization model which results from the occurrence of operations characterized by fixed mass load within the water network. The proposed iterative technique yielded a solution from which graphical representations based on the concept of limiting water profiles by Wang and Smith (1994) were developed. The strengths of the proposed technique lie in its ability to provide physical insights into the problem, numerical accuracy from mathematical modelling, to provide solution to large complex problems and also the ability to incorporate significant constraints such as flowrate and geographical constraints (Doyle & Smith, 1997).

It is noteworthy that, the above described techniques rely mostly on mathematical modelling to generate optimal water network results, which form the basis for the development of graphical representations. Therefore there exist no integration of the graphical and mathematical techniques and as such the benefits of hybridization are not fully exploited. To close this gap, authors such as Alva-Argaez et al. (1998), Mughees et al. (2013), Song et al. (2006) and Maria de Arruda et al. (2011) noticeably used graphical representations to initialize or rather simplify mathematical modelling. In particular, Mughees et al. (2013) investigated wastewater and freshwater minimization along with maximum water reuse/recycle using pinch analysis. The results obtained from this graphical technique were compared to those obtained from the mathematical programming. In this case, these techniques are compared and not integrated for purposes of obtaining optimum results.

Integration of the techniques is observed in the work of Alva-Argaez et al. (1998), who proposed a decomposition strategy based on a recursive procedure and integrated it within the optimization framework. In this case, water pinch principles are systematically integrated with the mathematical model. The proposed technique is called an automated design and the procedure is such that decomposition is applied on an MINLP problem, which is then distributed into a sequence of MILP problems solvable using branch and bound algorithm (Alva-Argaez, et al., 1998). The advantages of the proposed technique include the ability to accommodate practical constraints such as geographical and control constraints. Moreover, the technique yield designs of minimum total annualized costs (Alva-Argaez, et al., 1998).

Thereafter, Song et al. (2006) combined the water-oxygen pinch analysis with mathematical programming for wastewater treatment. Their hybrid system successfully decreased the number of uncertain parameters in the wastewater treatment superstructure. However, the technique is limited to the wastewater treatment system and not the total water network. Additionally, Maria de Arruda et al. (2011) used the water surplus diagram (WSD) to support the GAMS optimization software in a process of differentiated regeneration. Although they used the results from the WSD to initialize their model, their work does not involve a detailed regenerator design and therefore fail to capture the accurate cost of the regenerators along with optimal cost of the water network. The above extensive review highlights that there is a gap in literature for techniques which use an integrated approach of graphical and mathematical modelling techniques for the synthesis and design of optimal water and detailed regeneration networks.

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CHAPTER 3

Chapter 3 Methodology

3.1 Procedure for design of an integrated framework

The integrated framework begins with a graphical targeting technique as a preprocessing step for the mathematical model. This approach allows for rigorous designs to be achieved at faster convergence rates. The contribution of the preprocessing step is in reducing the number of variables of the superstructure, thereby enabling the mathematical model to effectively solve for the general optimal solution.

3.2 Graphical targeting: Improved Composite Table Algorithm

The graphical technique adopted in this work is called the Composite Table Algorithm (CTA) by Agrawal et al. (2006). The choice of which technique to adopt for this work was informed by the several advantages associated with CTA, such as its capabilities to handle both fixed flowrate and fixed load problems. As aforementioned, the technique combines graphical and algebraic characteristics, which offers both physical insights and accuracy in numerical analysis. The technique is enhanced to cater for partitioning type regenerators of unknown optimal performance prior to the design. Although CTA is inherently limited to a single contaminant system like many other pinch based techniques, it is applied in this work for multiple contaminant systems using the reference contaminant approach developed by Calixto et al. (2015). The flowsheet design technique adopted in this work is the Nearest Neighbour Algorithm (NNA) by Shenoy et al. (2012). The design technique provides simpler designs, reduces water flowrate throughout the network and help meet demand requirements at lower inlet concentrations than their threshold values.

3.2.1 Procedure for the Improved Composite Table Algorithm

The algorithm for the Improved CTA is shown in Figure 3.2.1. The algorithm is a modification of the Automated Composite Table Algorithm (ACTA) by Parand et al. (2016) and the Improved

Problem Table by Deng et al. (2016). A literature example of a fixed load problem by Wang & Smith (1994), is used to illustrate the procedure of the Improved CTA algorithm. The limiting data for this example is summarised in Table 3.2.1 below:

Table 3.2.1 Limiting data for the Fixed Load problem by Wang & Smith **(1994)**

Processes	**Limiting Flow (t/hr)**	C_{in}^{max}**(ppm)**	C_{out}^{max}**(ppm)**	**Mass load(g/hr)**
P1	20	0	100	2000
P2	100	50	100	5000
P3	40	50	800	30000
P4	10	400	800	4000
	C_e^{max}	200		
	C_{fw}	0		

In reference to the information provided in Table 3.2.1 above, the detailed description of the algorithm can be summarised in the following steps:

i) **Step 1**: In the first step, a vector of C_{perm} values is generated from the minimum concentration(C_{perm}^{min}) to the maximum concentration(C_{perm}^{max}). In this range, the minimum concentration is regarded as zero and the maximum concentration is the second minimum inlet concentration amongst all processes in the network. The motivation behind this choice is explained in section 3.2.2 below. In addition, an incremental step of 1 ppm was used to cater for many possible opportunities of an optimal C_{perm} in this range. All these efforts are taken due to the interdependence of freshwater, wastewater and regenerated flowrate on the value of C_{perm}. It is therefore important to explore most of the different possibilities of C_{perm} in order to attain optimal or near optimal results. Note: the subsequent steps are carried out at every value of C_{perm} in the vector.

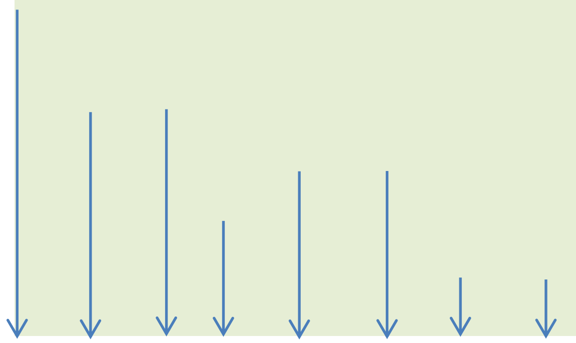
ii) **Step 2**: Locate all process sources and sinks as vertical lines with flowrates depicted at the bottom, in the first column of the Improved CTA. Then all their concentrations are arranged in an increasing order in the second column. This ordered arrangement of concentrations can be illustrated with Eq 3.1 below. The concentration of the freshwater source and the regenerator outlet concentration, C_{perm} are included in this arrangement. Note that an arbitrary value of 300 ppm is also added at the last entry to provide an end point for calculation and help with the construction of the last segment of the LCC (Deng, et al., 2016).

$$C_1 < C_2 < \cdots C_k < C_{arbitrary} \quad 3.1$$

The first two columns as explained in this step are illustrated in Table 3.2.2 below.

Table 3.2.2 Arrangement of flowrates and concentrations for process sources and sinks

Process Sources and Sinks	$\boldsymbol{C_k}$ $(\boldsymbol{ppm})$
	0
	20
	50
	100
	400
	800
	1000

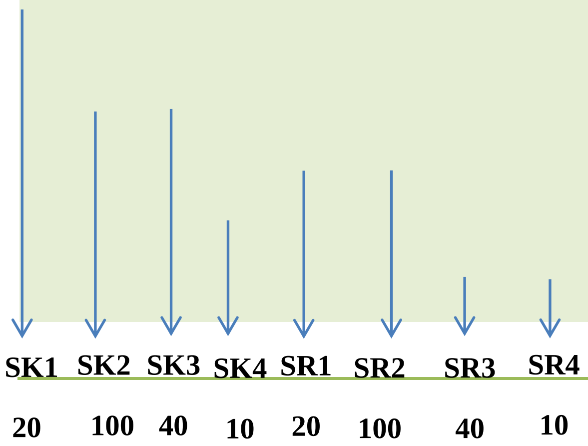


SK1	SK2	SK3	SK4	SR1	SR2	SR3	SR4
20	**100**	**40**	**10**	**20**	**100**	**40**	**10**

iii) **Step 3**: In the third step, the net flowrate (F_k^{net}) within each concentration interval is calculated in the third column. This flowrate is calculated as the difference between the total flowrates of all the process sources and that of sinks in that concentration interval. The net flowrate calculated in this step is included as an additional column to the data generated in Table 3.2.2 above. Therefore, the description of step 3 is demonstrated in Table 3.2.3 below:

Table 3.2.3 The net flowrate ($\boldsymbol{F_k}^{net}$) column

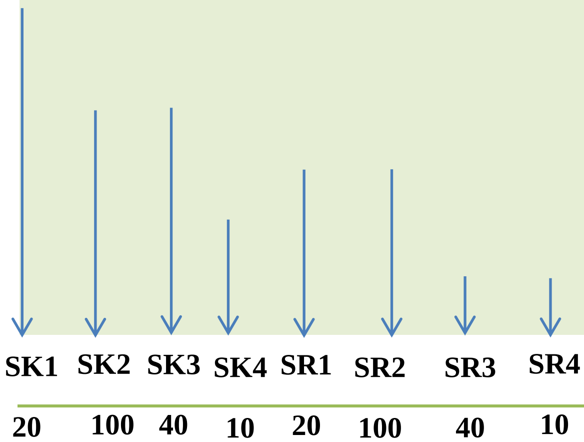
Process Sources and Sinks	C_k (ppm)	F_k^{net} (t/h)
	0	
	20	20
	50	20
	100	160
	400	40
	800	50
	1000	0



iv) **Step 4**: Then the net load ($\Delta m_k{}^{net}$) is calculated in the fourth column as the product of the net flowrate with the concentration difference of the corresponding interval. Additionally, the cumulative load ($\Delta m_k{}^{cum}$) is calculated in the fifth column and for the first entry, the value is zero as there is no load cumulated. This description is illustrated in Table 3.2.4 below:

Table 3.2.4 The additional fourth and fifth columns of the Improved CTA algorithm

Process Sources and Sinks	C_k (ppm)	F_k^{net} **(t/h)**	Δm_k^{net} **(g/h)**	Δm_k^{cum} **(g/h)**
	0		0	0
	20	20	400	400
	50	20	600	1000
	100	160	8000	9000
	400	40	12000	21000
	800	50	20000	41000
	1000	0	0	41000



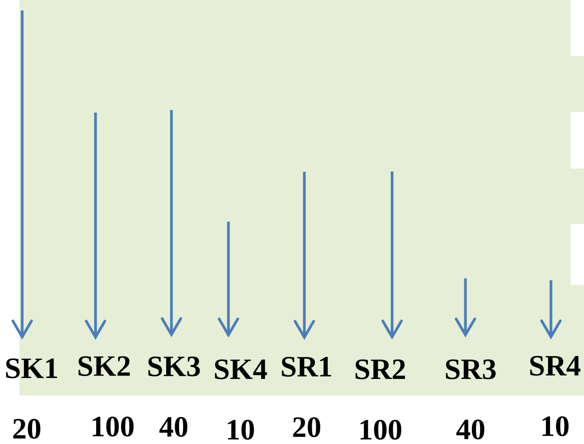
v) **Step 5**: In the 6th column, the freshwater flowrate is calculated at each concentration interval as illustrated in Table 3.2.5 below. The freshwater concentration in this case is assumed to be zero. The maximum value of freshwater in this column is regarded as the freshwater target at that specific regenerator outlet concentration.

vi) **Step 6**: In the 7th and 8th columns, the regenerated water flowrate required in the system $(F_{TU1,sys})$ and the pre-regeneration concentration (C_{reg}) are calculated, respectively. The 7th and 8th columns, along with a table for feasibility evaluation complete the procedure for the Improved CTA algorithm, as depicted in Table 3.2.6 below:

Table 3.2.5 The overall table of the Improved CTA algorithm

C_k (ppm)	F_k^{net} (t/h)	Δm_k^{net} (g/h)	Δm_k^{cum} (g/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	C_{reg} (ppm)
0		0	0	0	**41.32**	
20	20	400	400	20	0	
50	20	600	1000	20	0	
100	160	8000	9000	90	**60.86**	62.65
400	40	12000	21000	52.5	11.17	58.79
800	50	20000	41000	51.25	10.19	**92.79**
1000	0	0	41000	41	-0.32	11.91

Process Sources and Sinks



F_{tu1}^{in} (t/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	F_{loss} (t/h)	C_{reg} (ppm)
102.17	41.32	60.86	0	92.79
F_{perm} **(t/h)**	C_{perm} **(ppm)**	F_{rej} **(t/h)**	C_{rej} **(ppm)**	$F_{tu1,e}^{prod}$ **(t/h)**
76.63	20.00	25.54	311.15	15.77
$F_{tu1,e}$ **(t/h)**	C_e^{mix} **(ppm)**	ΔC_e	**Error**	**%*RR***
41.32	200	0	1.00	83.83

As stated above, feasibility evaluations are also carried out in this step, using Excel Goal Seek to minimize ΔC_e to zero. This ΔC_e is the difference in concentration between the concentration of the discharged wastewater and that of the environmental limit. A successful minimization of ΔC_e is one without any negative flowrates in the table of the Improved CTA, as these are associated with mass load infeasibilities. Therefore, this procedure is carried out for every outlet concentration of the regenerator(C_{perm}), from which feasible flows of freshwater, regenerated water and consequently wastewater flows are determined.

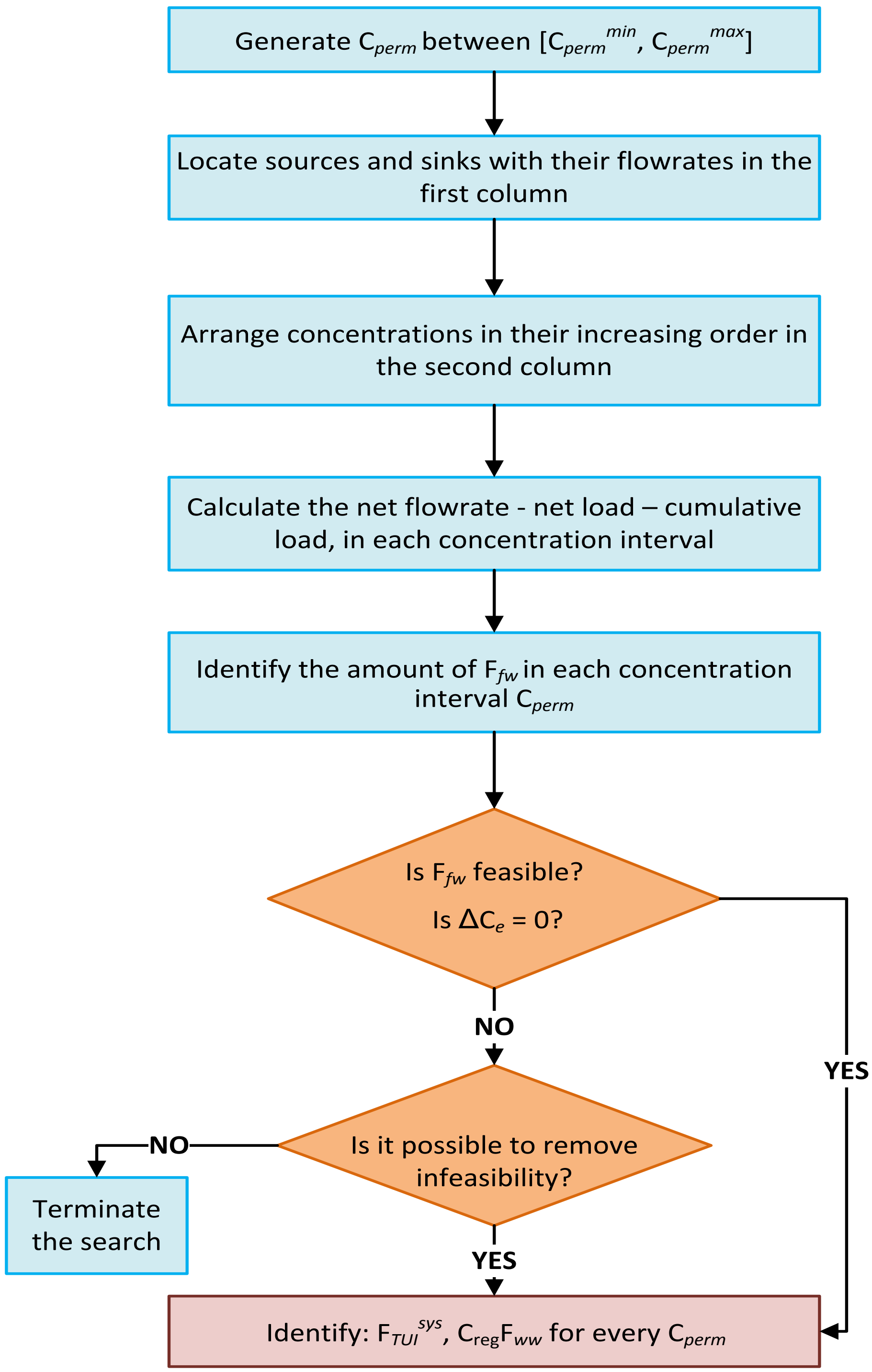


Figure 3.2.1 An algorithm for the Improved CTA

3.2.2 The algebraic calculations for the Improved CTA algorithm

The major contributions of this algorithm include proper calculations of the pre-regeneration concentration (C_{reg}) for a partitioning type regenerator, given by Eq 3.2. The benefits are improvements in the freshwater and wastewater flow targets, coupled with an optimal Removal Ratio (*RR*) obtained for the regenerator. Moreover, incorporating the environmental discharge constraint in the algorithm reduces the search space for an optimal post-regeneration concentration (C_{perm}), from which an optimal RR is calculated using Eq 3.5. The search is thus terminated when a specific C_{perm} yields negative flowrates in the table and consequently infeasible solution. In the case of multiple contaminants in the water network, the algorithm is applied on the selected reference contaminant.

According to Bai et al. (2007) and Wang & Smith (1994), an optimal C_{perm} need not to be higher than the second minimum concentration of the limiting inlet concentration of all the processes in the network, but higher than the minimum concentration in the network. Additionally, C_{perm} is targeted by carrying out a cost analysis, wherein a trade-off between the operational costs and the capital costs is determined. In this case, the operational cost refers to the freshwater cost and is given by Eq 3.4 while the capital cost refers to the cost of regeneration, given by Eq 3.3. The total network cost is thus calculated using Eq 3.6 below.

$$C_{reg} = \frac{\Delta m_k{}^{cum} - F_{fw}\,(C_k - C_{fw}) + (F_{perm} \times C_{perm})}{F_{TU1,in}} \qquad 3.2$$

$$CR = \alpha \times \left(\frac{C_{perm}{}^{max}}{C_{perm}}\right)^{\gamma} \times (F_{TU1}{}^{sys})^{\beta} \qquad 3.3$$

$$CF = \mu_{Fw} \times F_{fw} \qquad 3.4$$

$$RR = \frac{F_{rej} \times C_{rej}}{F_{TU1,in} \times C_{reg}} \qquad 3.5$$

$$CT = CF + CR \qquad 3.6$$

These cost functions are adapted from Parand et al. (2016), wherein the unit cost of freshwater (μ_{Fw}) is assumed to be 1$/ton and the value of the annual operating hours is taken as 8600 hr/yr. Moreover, the coefficients of β and γ are set at 0.14 and 1.75, respectively. However, the disposal cost is eliminated in the total network cost as the algorithm developed in this work involves adherence to the environmental discharge limit. The objective here is to determine the best total cost (CT) of the water network; that which allows for better combination of the operational and regeneration cost. The choice of the best CT i.e. that which corresponds to an optimum C_{perm} is facilitated by minimum freshwater consumption and the reusability of the regenerated water in operations without violations of the maximum inlet concentrations to those specific operations. Essentially, the regenerated water flowrate should not be too high and exceed the handling capacity of the operations, as this can lead to mass exchange network infeasibilities (Delgado, et al., n.d.). As a result, an optimum C_{perm} is located such that minimum flow targets of freshwater, wastewater and regenerated water are attained prior to the detailed design of the water network.

3.3 Mathematical model

The material balances for water operations within the water network are formulated following the superstructure representation depicted in Figure 3.2. This representation is adapted from the work of Khor et al. (2011). The superstructure represents every possible combination between the processing units, and this includes the sources, *J*, the sinks, *I*, and the regenerator represented by unit *R*. In the case of a fixed flowrate approach, the water using processes are considered as the sinks and the sources are units which generate water. As illustrated in Figure 2, the sources can be allocated directly to the sinks or partially treated in the regenerator before feeding the sinks. The results from the mathematical formulation provide the minimum cost of the network along with the best possible configuration of the water network. The MINLP model is developed based on the superstructure representation in Figure 3.3.1 below. In addition, a schematic representation of the hollow fibre reverse osmosis membrane (HFRO) is depicted in Figure 3.3.2 to clarify the model equations. The following equations are for the mathematical formulation and are adapted from the work of Khor et al. (2011).

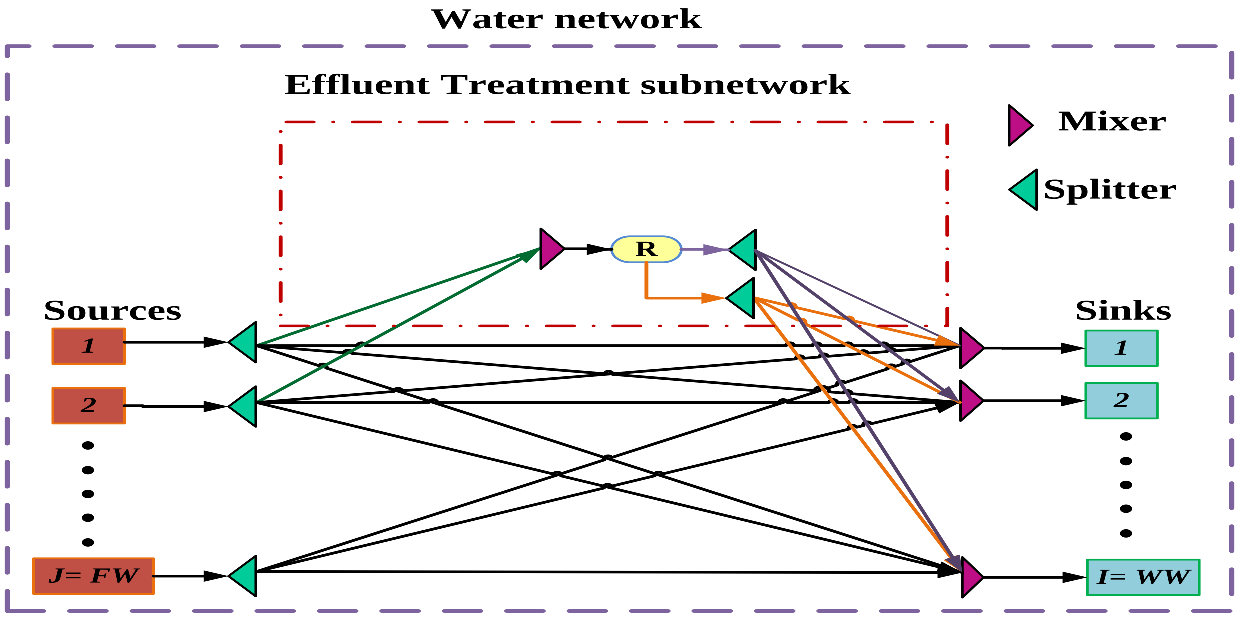


Figure 3.3.1 Superstructure representation of the water network

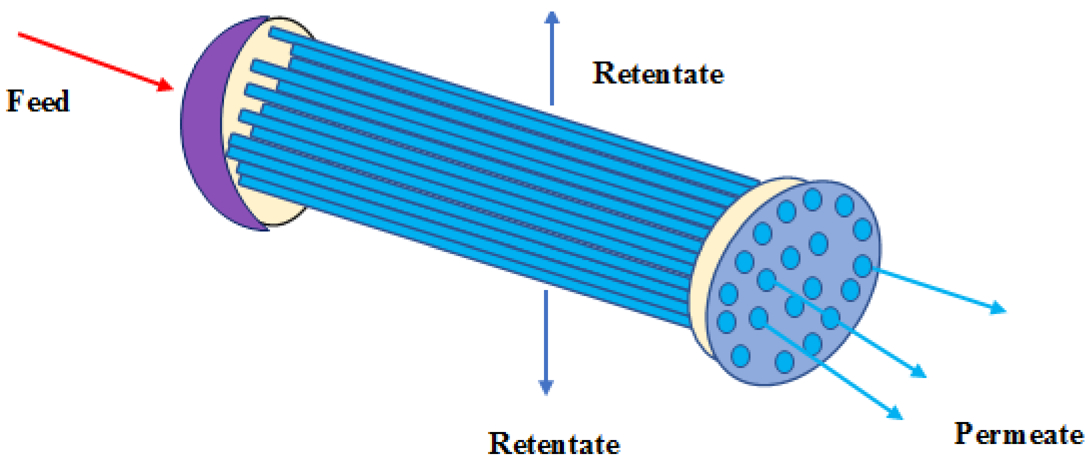


Figure 3.3.2 Schematic representation of a HFRO membrane

3.3.1 Water balances

The water balances are based on the representation shown in Figure 3.3.1 above. These balances are generated for the sources, sinks and the regeneration unit. In the case of sources, every given source has an option to send water for reuse/ recycle in the sink without violating the concentration limit of that sink. Moreover, water can be sent for purification in the regeneration unit so that it qualifies for reuse in the sinks. The flow balance is therefore modelled as follows:

$$Q_1(so) \geq \sum_{int\,\in\,INT} Q_d(so,int) + \sum_{si\in\,SI} Q_a(so,si) \qquad \forall\ \text{so} \in \text{SO} \qquad 3.7$$

Although a single regenerator is modelled in this work, equation 3.7 is simply generic and illustrates that the concept is applicable to multiple regenerators. In addition, the inequality sign used in equation 3.7 caters for the excess amount of water (termed the effluent) that is sent for wastewater treatment.

Furthermore, the flow balance for the regeneration unit is dependent on the water supplied by the sources. This unit receives a mixture of water from the sources and then generate streams of permeate and retentate, which are further allocated to the sinks. The formulation of such a balance is as follows:

$$\sum_{so\,\in\,SO} Q_d(so,int) = \sum_{si\in SI} Q_{b,perm}(int,si) + \sum_{si\,\in\,SI} Q_{b,rej}(int,si)$$
$$\forall\ int \in \text{INT} \qquad 3.8$$

Lastly, the water balance for the sinks is the summation of water from the source streams and either permeate or retentate stream of the regeneration unit. The flow balance for the sinks is modelled as follows:

$$Q_2(si) = \sum_{so\in\,S0} Q_a(so,si) + \sum_{int\,\in\,INT} \left(Q_{b,perm}(int,si) + Q_{b,rej}(int,si)\right)$$

$$\forall\ si \in \text{SI} \qquad 3.9$$

3.3.2 Design equations

The type of regenerator modelled in this work is reverse osmosis (RO). Liquid recovery (α) and removal ratio (*RR*) are the performance indices or design equations commonly used for the RO regenerator. Liquid recovery refers to the amount of the feed flowrate into the regenerator that exits as the permeate stream while the *RR* refers to the fraction of the inlet mass load that exits as the retentate stream of the regenerator. The constraints for the liquid recovery and the removal ratio are represented by equation 3.10 and 3.11, respectively.

$$\alpha(int) = \frac{\sum_{si\in SI} Q_{b,perm}(int,si)}{\sum_{so\,\in\,SO} Q_d(so,int)} \qquad 3.10$$

$$RR = \frac{C_{rej}(int,co)\sum_{si\,\in\,SI} Q_{b,rej}(int,si)}{\sum_{so\,\in\,SO} Q_d(so,int) C_{so}(int,co)} \qquad \forall\ \text{int} \in \text{INT},\ \ \forall\ \text{co} \in \text{CO} \qquad 3.11$$

In reference to equation 3.10, the complement of the liquid recovery$(1 - \alpha)$ is discharged as the retentate stream.

3.3.3 Constraint for forbidden mixing in the sinks

The mixing of the permeate and the retentate stream of the regeneration unit in the same sink is not allowed because each sink can only tolerate up to a maximum allowable concentration limit, $C_{max}(si, co)$. It is important that that this limit is not violated for operational efficiency of each sink. The constraint that forbids mixing in the sinks is thus represented as follows:

$$Y_{b,perm}(int, si) + Y_{b,rej}(int, si) \leq 1 \qquad \forall \text{ int} \in \text{INT} \qquad 3.12$$

Moreover, the component concentration balance for the sink is given as follows:

$$Q_2(si) \times C_{max}(si, co) \geq \left(\sum_{so \in SO} Q_a(so, si) \times C_{so}(so, co)\right) + \left(\sum_{int \in INT} C_{perm}(int, co) \times Q_{b,perm}(int, si)\right) + \left(\sum_{int \in INT} C_{rej}(int, co) \times Q_{b,rej}(int, si)\right)$$

$$\forall \text{ si} \in \text{SI}, \ \forall \text{ co} \in \text{CO} \qquad 3.13$$

Note that, included part of these sinks is a wastewater sink which is discharged to the environment at acceptable standards. Therefore, information known about this sink prior to design is the environmental discharge limit which must be observed to avoid penalties. Only the flowrate of this sink is a variable and thus determined upon optimization of the water network.

3.3.4 Component concentration balance for the regeneration unit

Similarly to the sinks, there is also a component balance for the regeneration unit and this is modeled as follows:

$$\sum_{so \in SO} Q_d(so, int) . C_{so}(so, co) = \sum_{si \in SI}\{Q_{b,perm}(int, si) . C_{perm}(int, co)\} + \sum_{si \in SI}\{Q_{b,rej}(int, si) . C_{rej}(int, co)\}$$

$$\forall \text{ si} \in \text{SI}, \ \forall \text{ co} \in \text{CO} \qquad 3.14$$

3.3.5 Constraints on Reverse Osmosis (RO) operating conditions

These constraints are put in place to capture the characteristics and complexities in the mechanistic model of the RO membrane (Khor, et al., 2011). These constraints are generated for the RO feed pressure (P_F) and the average contaminant concentration in the shell side, C_s.

$$P_F = \Delta P + \left(\frac{\Delta P_{shell}}{2} + P_P\right) \quad 3.15$$

Where,

$\Delta P = (P_F + P_R)/2 - P_P$; $\Delta P_{shell} = P_F - P_R$; $\Delta P = \left(\frac{N_{water}}{A\gamma}\right) + \frac{\pi_F}{C_F(int,co))C_S}$; $N_{water} = \frac{N_{solute}}{\left(C_{perm}(int,si)\right)}$;

$N_{solute} = \left(\frac{D_{2M}}{K\delta}\right) C_S$; $C_S = \frac{C_F + C_{rej}}{2}$

In order to define P_F in terms of contaminant concentration in the feed stream of the regeneration unit (C_F) and C_{perm}, the average concentration in the shell side (C_s) is used. The constraint for C_s is thus written as follows:

$$C_S = \frac{C_f + C_{rej}}{2} = \frac{2Q_F C_F - Q_{b,perm} C_{perm} - Q_{b,perm} C_F}{2(Q_F - Q_{b,perm})} \quad 3.16$$

3.3.6 The total annualized cost formulation

The total annualized cost (TAC) takes into account the capital costs of the RO modules, pumps and the turbine. There is also consideration of the operating costs for the pump and pretreatment chemicals. Since the turbine recovers kinetic energy from the high pressure retentate stream (Saif, et al., 2008), the operating revenue of the energy recovered is also incorporated within the TAC formulation. To minimize the complex nature of the TAC constraint, the expression is formulated independent of the contaminant type. The following are some key equations used to formulate the TAC expression:

$$\Delta\pi_{RO} = OS \times \sum_{co} C_{F,average}(RO, co) \quad 3.17$$

Where OS refers to the proportionality constant between the osmotic pressure and the average solute concentration on the feed side.

The constraint represented by equation 3.17 above is for the osmotic pressure on the retentate side of the regenerator. In this case, only the osmotic pressure on the retentate side is considered because the contaminant concentration of the permeate stream is significantly lower than that of the feed side. The following equation describes the feed side contaminant concentration.

$$\sum_{co \in CO} C_{F,average}(RO, co) = \frac{\sum_{co \in CO} C_{Perm}(RO,co) \times A(\Delta P - \Delta\pi_{RO})\gamma}{K_c(co)} \quad 3.18$$

Where K_c refers to the contaminant permeability coefficient.

Furthermore, the relation for the permeate flowrate is described as follows:

$$Q_p = N_m.A.S_m.\gamma(\Delta P - \Delta\pi_{RO}) \quad 3.19$$

Where, N_m refers to the number of modules.

These key equations lead to the following formulation of TAC:

$$TAC = C_{module} \times \left(\frac{\sum_{si \in SI} Q_{b,perm}(int,si)}{A.S_m.\gamma\left(P_F - \left(\frac{\Delta P_{shell}}{2} + P_p\right) - \frac{OS.\sum_{co \in CO} C_{Perm}(RO,co) \times A\left(P_F - \left(\frac{\Delta P_{shell}}{2} + P_p\right) - \Delta\pi_{RO}\right)\gamma}{K_C} \right)} \right) +$$

$$\left(C_{pump}\left(POWER_{pump}\right)^{0.65}\right) + (C_{turbine}(POWER_{turbine})^{0.43}) +$$

$$\left(C_{electricity}.AOT.\left(\frac{POWER_{pump}}{\eta_{pump}}\right)\right) + (C_{chemical}.AOT \times \sum_{so \in SO} Q_d(so,int) -$$

$$(C_{electricity}.AOT.POWER_{pump}.\eta_{pump}) \quad 3.20$$

Where,

$$q_p(co) = S_m A \left\{P_F - \left(\frac{\Delta P_{shell}}{2} + P_p\right) - \frac{\pi_F}{2}\left(1 + \frac{C_{rej}(int,co)}{C_F(int,co)}\right)\right\}\gamma \quad 3.21$$

$$POWER_{pump} = \sum_{so \in SO} Q_d(so,int)(P_F - P_{atm)}(1.01325 \times 10^5) \quad 3.22$$

$$POWER_{turbine} = \sum_{si \in SI} Q_{b,rej}(so,int)(P_R - P_{atm)}(1.01325 \times 10^5) \quad 3.23$$

3.3.7 The big-M logical constraints

In order to determine the existence of stream piping interconnections, logical constraints and discrete binary variables are used. These constraints are used in association with fixed cost charge that is penalized in the objective function for the 0-1 variables. In this case, if a variable takes a value of zero, the associated flowrate must be zero. However, if the variable takes on a value of 1, it means e.g. that particular piping interconnection exists and therefore has a non-zero flowrate. The big-M parameter is thus used to formulate these logical constraints, in which M can be a valid upper bound (denoted by subscript "U") or lower bound (denoted by subscript "L"). In this context, any piping interconnection with flowrate below the lower bound is discarded from the final design. Presented in constraint 3.24-3.27 are the big-M logical constraints for various piping interconnections.

$$M_a^L(so,si).Y_a(so,si) \leq Q_a(so,si) \leq M_a^U(so,si).Y_a(so,si) \qquad 3.24$$

$$M_{b,perm}^L(so,si).Y_{b,perm}(so,si) \leq Q_{b,perm}(int,si) \leq M_{b,perm}^U(so,si).Y_{b,perm}(so,si) \qquad 3.25$$

$$M_{b,rej}^L(so,si).Y_{b,rej}(so,si) \leq Q_{b,rej}(int,si) \leq M_{b,rej}^U(so,si).Y_{b,rej}(so,si) \qquad 3.26$$

$$M_d^L(so,int).Y_d(so,int) \leq Q_d(so,int) \leq M_d^U(so,int).Y_d(so,int) \qquad 3.27$$

3.3.8 Variable bounds

There are constrains termed variable bounds, which are placed on the lower and upper bounds of some specific variables in order to properly represent the water network problem. These variables include the total feed flowrate into the regenerator $Q_F(int)$, the RO osmotic pressure on the retentate side $\Delta\pi_{RO}$ and the RO feed pressure P_F. The constraints for these variables are presented in equation 3.28-3.30 below:

$$Q_F^L(int) \leq Q_F(int) \leq Q_F^U(int)$$

Where, $Q_F(int = \sum_{so \in SO} Q_d(so,int)$ $\qquad \forall$ int ∈ INT 3.28

$$\Delta\pi_{RO}{}^L \leq \Delta\pi_{RO} \leq \Delta\pi_{RO}{}^U \qquad 3.29$$

$$P_F^L \leq P_F \leq P_F^U \qquad 3.30$$

3.3.9 The objective function

The aim with the objective function is to minimize the overall water regeneration network cost on an annualized basis. The cost components embedded within this function include:

(i) The freshwater cost;
(ii) The treatment cost of wastewater;
(iii) TAC of the RO network
(iv) Capital and operating costs of the piping interconnections

In terms of the piping costs, a linear fixed-charge cost model is assumed. In this cost model, the big-M logical constraints described above play a major role. In particular, these constraints help reduce the number of piping interconnections by discarding flowrates below the threshold value, and thereby reducing the piping costs. In addition, these pipes are assumed to share the same properties of parameters *p*, *q*, *v*, and the 1-norm Manhattan distance *D*. Furthermore, the piping cost include the approximate length and material of construction for these pipes. In summary, the constraints described in equations 3.7 - 3.30 resulted into a nonconvex MINLP model formulation with the following objective function:

$$\text{Obj} = \min\ \left(C_{water} \sum_{si \in SI} Q_a(freshwater, si) + C_{waste} Q_2(waste)\right) \text{AOT} + \sum_{co \in CO} TAC(co) + \left(\frac{m(1+m)^n}{(1+m)^n - 1^n}\right) \left(\sum_{so \in SO} \sum_{si \in SI} D_a(so, si) \left(\frac{p.Q_a(so,si)}{3600v} + q.Y_a(so, si)\right)\right) + \left(\sum_{int \in INT} \sum_{si \in SI} D_{b,perm}(int, si) \left(\frac{p.Q_{b,perm}(int,si)}{3600v} + q.Y_{b,perm}(in, si)\right)\right) + \left(\sum_{int \in INT} \sum_{si \in SI} D_{b,rej}(int, si) \left(\frac{p.Q_{b,rej}(int,si)}{3600v} + q.Y_{b,rej}(int, si)\right)\right) + \left(\sum_{int \in INT} \sum_{si \in SI} D_d(so, int) \left(\frac{p.Q_d(so,int)}{3600v} + q.Y_d(so, int)\right)\right) \quad 3.31$$

3.3.10 Nomenclature:

(i) Nomenclature for the mathematical model

Sets

SO = {so|so = water sources}

SI = {si|si = water sinks}

INT = {int|int = regeneration unit}

CO = {co|co = contaminants}

Parameters

A= water permeability coefficient

AOT = annual operating time

$C_{max}(so, co)$ = maximum allowable contaminant concentration co in sink si

$C_{so}(so, co)$= contaminant concentration co in source stream so

$C_{chemical}$ = unit cost of pre-treatment chemicals

C_{waste}= unit cost for wastewater treatment

$C_{electricity}$= unit cost of electricity

C_{module}= unit cost of HFRO membrane module

C_{pump}= cost coefficient for pump

$C_{turbine}$= cost coefficient for turbine

$D_{2M}/K\delta$= solute (contaminant) flux constant

K_c= solute (contaminant) permeability coefficient

m=fractional interest rate

$M_a(so, si)$= big-M constant for interconnection between source so to sink si

$M_{b,perm}(int, si)$= big-M constant for interconnection between regeneration unit int to sink

$M_{b,rej}(int, si)$= big-M constant for interconnection between regeneration int to sink si

$M_d(so, int)$= big-M constant for interconnection between source so to regeneration unit int

n=number of years

OS= osmotic coefficient

P_F= feed pressure of regeneration unit

P_P= permeate pressure of regeneration unit

p, q= parameter for carbon steel piping cost based on Chemical Engineering Plant Cost Index (CEPCI)

$POWER_{pump}$= pump power

$POWER_{turbine}$=turbine power

$Q_1(so)$= flowrate of sources

$Q_2(si)$= flowrate of sinks

RR= removal ratio

S_m= membrane area module

α=liquid phase recovery

μ= viscosity of water

Continuous variables

$C_F(int, co)$= concentration of contaminant co in feed stream of regeneration unit int

$C_{perm}(int, co)$= concentration of contaminant co in permeate stream of regeneration unit

$C_{rej}(int, co)$= concentration of contaminant co in reject stream of regeneration unit int

$C_s(int, co)$= concentration of contaminant co in shell side of regeneration unit int

$C_{so}(so, co)$= contaminant concentration co in source so

$Q_a(so, si)$= allocated flowrate between source so and sink si

$Q_{b,perm}(int, si)$= allocated flowrate between permeate stream of regeneration unit and sink

$Q_{b,rej}(int, si)$= allocated flowrate between reject stream of regeneration unit and sink si

$Q_d(so, int)$= allocated flowrate between source so and regeneration unit int

$Q_F(int)$= total feed flowrate into regeneration unit int

N_{solute}= solute flux through the HFRO membrane

N_{water}= water flux through the HFRO membrane

P_R= retentate pressure from regeneration unit

q_P= permeate flowrate per HFRO module

TAC= total annualized cost

$\Delta\pi$RO= osmotic pressure on HFRO module

Binary 0-1 variables for the existence of stream piping interconnections

$Y_a(so, si)$= between source so and sink si

$Y_{b,perm}(int, , si)$= between permeate stream of regeneration unit int and sink si

$Y_{b,rej}(int, , si)$= between retentate stream of regeneration unit int and sink si

$Y_d(so, int)$= between source so and regeneration unit int

(ii) Nomenclature for the Improved CTA algorithm

$\Delta m_k{}^{cum}$= cumulative load

$\Delta m_k{}^{net}$= net load in each concentration interval

ΔC_e = the environmental discharge limit

F_{fw}= freshwater flowrate

C_{fw}, C_{perm}= concentration of freshwater and regenerator permeate concentration, respectively

C_{SK}, C_{SR}= concentration of the sources and sinks, respectively.

C_K= concentration within each interval

C_{reg}= pre-regeneration concentration

F_{perm}= flowrate for the regenerator permeate

$F_{TU1,in}$= feed flowrate to the regenerator

$F_{TU1,sys}$= regenerated water flowrate required in the water-using system

$F_k{}^{net}$= the net flowrate within each concentration interval

β, α, γ= cost coefficients

μ_{Fw}= unit cost coefficient for freshwater

SR= process sources

SI= process sinks

3.4 References

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CHAPTER 4

Chapter 4 Results and Discussion

4.1 Introduction

This chapter demonstrates the applicability of the proposed Improved Composite Table Algorithm on three literature examples of fixed load problem, fixed flowrate problem, and multiple contaminant problems. The algorithm is further applied on an industrial case study of a fixed flowrate water network. The results of the graphical targeting technique are presented first and then followed by those of the integrated framework (graphical and mathematical modelling hybridization). The benefits of the integrated framework are clearly revealed when the different scenarios are considered. These scenarios will be discussed in detail under the integrated framework section.

4.2 Illustrative examples

4.2.1 Application of the Improved CTA on a fixed load problem

In order to illustrate the algorithmic procedure developed in this work, it is applied on a fixed load literature example from the work of Wang & Smith [10]. The limiting data for the water network is shown in Table 4.2.1.

Table 4.2.1 Limiting data for the Fixed Load problem by Wang & Smith (Wang & Smith, 1994)

Processes	Limiting Flow (t/hr)	$C_{in}{}^{max}$(ppm)	$C_{out}{}^{max}$(ppm)	Mass load(g/hr)
P1	20	0	100	2000
P2	100	50	100	5000
P3	40	50	800	30000
P4	10	400	800	4000
	$C_e{}^{max}$	200		
	C_{fw}	0		

Next, the basic flowrate targeting equations are illustrated and the results obtained are summarised in Table 4.2.2 below. In reference to the Algorithm for the Improved CTA, the net flowrate in the 3rd column of Table 4.2.2 is calculated using Eq.4.1 while the net load in the 4th column is calculated using Eq.4.2. The net flowrate is the flow difference between the sinks and the sources within each concentration interval and this is calculated based on the process allocation in column 1.

$$F_k^{net} = \sum_j F_{SKj} - \sum_i F_{SRi} \qquad \forall \; C_{SKj}, C_{SRi} \le C_k \qquad (4.1)$$

$$\Delta m_k^{net} = F_k^{net}(C_k - C_{k-1}) \qquad \forall \; k > 1 \qquad (4.2)$$

Furthermore, the freshwater flow is calculated for each concentration interval using Eq.4.3 and the maximum value is taken as the freshwater target for a direct reuse and recycle of water without integration of the regeneration unit. The maximum value is selected because the higher the freshwater flow, the lower will be the slope of the water supply line (WSL) and the less likelihood of this line crossing the limiting composite curve and yielding mass exchange infeasibilities. Next, the amount of regenerated water to be used in the system is calculated using Eq. 4.4, from which the flow target is also taken as the maximum value in the column for the same reason as in the case of freshwater. This regenerated flow is calculated from the concentration interval greater than C_{perm} as the difference between C_k and C_{perm} cannot be equal to zero. Then an optimal pre-regeneration concentration (C_{reg}) in column 10 of Table 4.2.2 is calculated using Eq.4.5, from which a maximum value of 92.79 ppm was calculated and this is lower than the direct reuse and recycle pinch concentration of 100 ppm. Due to the interdependence of the flow targets on the C_{reg}, it is illustrated in this work that the calculation of an optimum C_{reg} contributes to the determination of accurate flow targets for the water network than when this key parameter is fixed at the direct reuse/recycle pinch concentration (Cpr).

$$F_{fw} = \frac{\Delta m_k^{cum}}{C_k - C_{fw}} \qquad \forall \; C_{FW} < C_k \le C_{arbitrary} \qquad (4.3)$$

$$F_{TU1,sys} = \frac{\Delta m_k^{cum} - F_{fw}(C_k - C_{fw})}{(C_k - C_{perm})} \qquad \forall \; C_{perm} < C_k \le C_{arbitrary} \qquad (4.4)$$

$$C_{reg} = \frac{\Delta m_k{}^{cum} - F_{fw}\,(C_k - C_{fw}) + (F_{perm} \times C_{perm})}{F_{TU1,in}} \qquad (4.5)$$

To get the feed flowrate into the regenerator ($F_{tu1}{}^{in}$), Eq.4.6 is used. This flowrate is calculated as the difference between the water allocated in the water-using system and the water lost from the system. The water lost from the water using system can be calculated using Eq.4.7. Since a partitioning type regenerator is used, the regenerator feed flowrate is distributed into the permeate stream and the reject stream, as illustrated in Eq.4.8. Then, the permeate stream is distributed into the water to be reused/recycled in the water using processes ($F_{TU1,sys}$) and the water to be discharged to the wastewater sink ($F_{tu1,e}{}^{prod}$) for dilution, using Eq.4.9. The wastewater flowrate is calculated as the summation of the reject stream and the portion of the permeate stream discharged into the wastewater sink, using Eq.4.10.

$$F_{tu1}{}^{in} = (F_{fw} + F_{TU1,sys}) - F_{sys}{}^{loss} \qquad (4.6)$$

$$F_{sys}{}^{loss} = \sum_j^{Nsk} F_{SKj} - \sum_i^{Nsr} F_{SRi} \qquad (4.7)$$

$$F_{tu1}{}^{in} = F_{perm} + F_{rej} \qquad (4.8)$$

$$F_{perm} = F_{TU1,sys} + F_{tu1,e}{}^{prod} \qquad (4.9)$$

$$F_{tu1,e} = F_{rej} + F_{tu1,e}{}^{prod} \qquad (4.10)$$

Feasibility check is also ensured using Eq.4.11 so that the contaminant concentration of the discharged wastewater ($C_e{}^{mix}$) into the environment does not exceed the maximum discharge limit ($C_e{}^{MAX}$) given by the environmental legislation. The concentration of the wastewater mixture is calculated using Eq.4.12.

$$\Delta C_e = C_e{}^{mix} - C_e{}^{MAX} \qquad (4.11)$$

$$C_e{}^{mix} = \frac{(F_{rej} \times C_{rej}) + (F_{tu1,e}{}^{prod} \times C_{perm})}{F_{tu1,e}} \qquad (4.12)$$

Table 4.2.2 The Improved Composite Table Algorithm (CTA) at $C_{reg} \neq Cpr$

Process Sources and Sinks	C_k (ppm)	$F_k{}^{net}$ (t/h)	$\Delta m_k{}^{net}$ (g/h)	$\Delta m_k{}^{cum}$ (g/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	C_{reg} (ppm)
	0		0	0	0	**41.32**	
	20	20	400	400	20	0	
	50	20	600	1000	20	0	
	100	160	8000	9000	90	**60.86**	62.65
	400	40	12000	21000	52.5	11.17	58.79
	800	50	20000	41000	51.25	10.19	**92.79**
	1000	0	0	41000	41	-0.32	11.91

SK1	SK2	SK3	SK4	SR1	SR2	SR3	SR4
20	100	40	10	20	100	40	10

$F_{tu1}{}^{in}$ (t/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	F_{loss} (t/h)	C_{reg} (ppm)
102.17	41.32	60.86	0	92.79
F_{perm} (t/h)	C_{perm} (ppm)	F_{rej} (t/h)	C_{rej} (ppm)	$F_{tu1,e}{}^{prod}$ (t/h)
76.63	20.00	25.54	311.15	15.77
$F_{tu1,e}$ (t/h)	$C_e{}^{mix}$ (ppm)	ΔC_e	**Error**	**%*RR***
41.32	200	0	1.00	83.83

Upon applying the Improved CTA on the problem given in Table 4.2.1, an optimal flow target of 41.32 t/hr was obtained for freshwater and similarly for the wastewater as this is a fixed load problem. The targets are used to illustrate the feasibility of the CTA technique, with the water supply line (WSL) completely below the limiting composite curve (LCC), as shown in Figure 4.2.1. Note that the second graph in Figure 4.2.1 is the enlargement of the circled region in the first graph. In reference to Figure 4.2.2, the best cost was found at a *Co* or C_{perm} value of 20 ppm, which allows reusability of the regenerated water even within the operation with the 2nd

lowest maximum inlet concentration. It can further be observed from Figure 4.2.2 that the regeneration cost increases with a decrease in the post-regeneration concentration (C_{perm}); therefore fixing C_{perm} may lead to suboptimal results as it can be either over-estimated or under-estimated.

Moreover, the regenerator RR is a function of C_{reg}, a variable that is largely dependent on the determination of an optimum C_{perm} as illustrated in Eq.4.5. Therefore, the interdependence of these key parameters (C_{perm} , C_{reg}, RR) justifies the search for optimal regenerator performance as the results obtained significatly affect the flow targets to be determined for the water network.

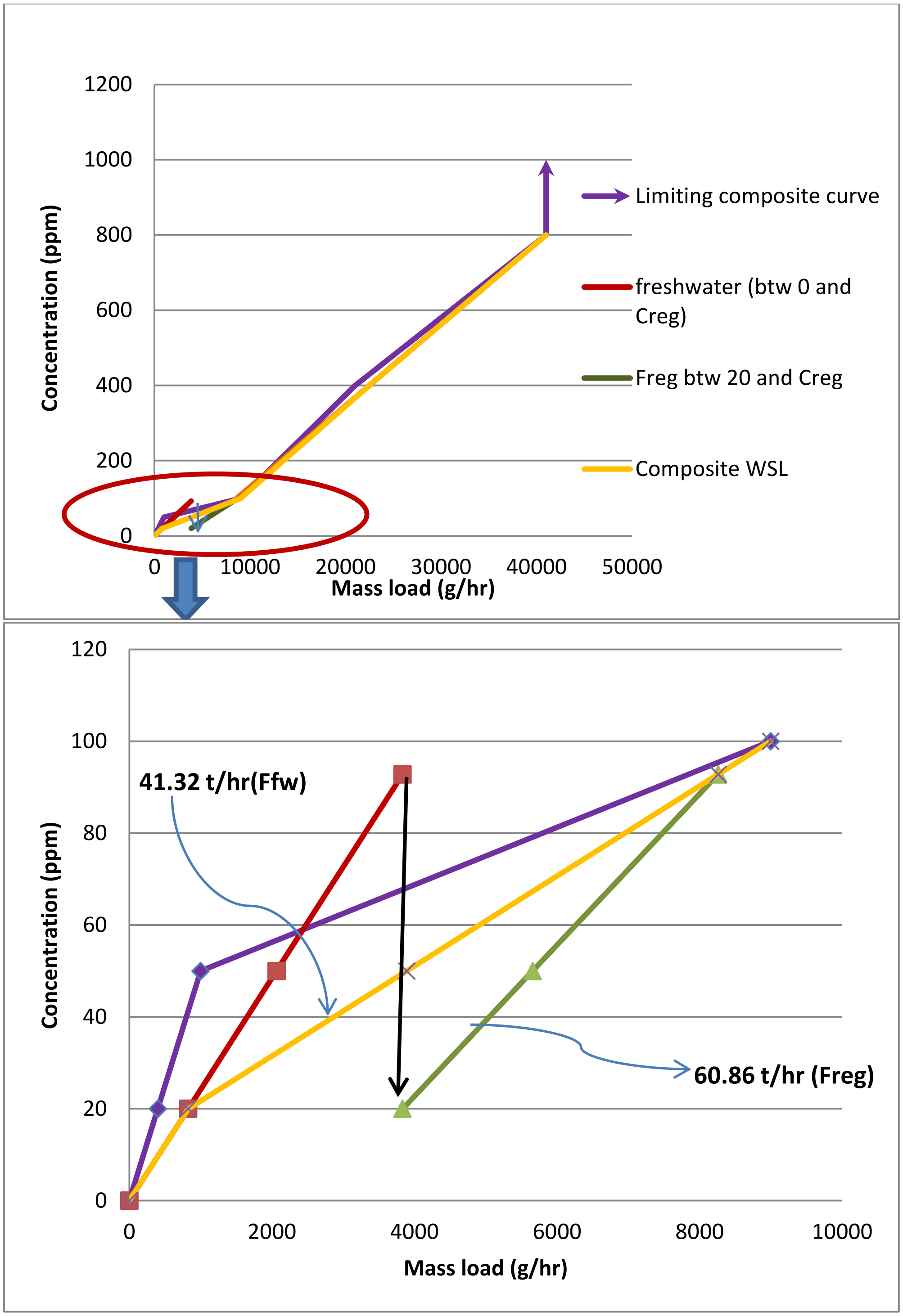


Figure 4.2.1 The graphs of Limiting Composite curve along with the Water Supply Line

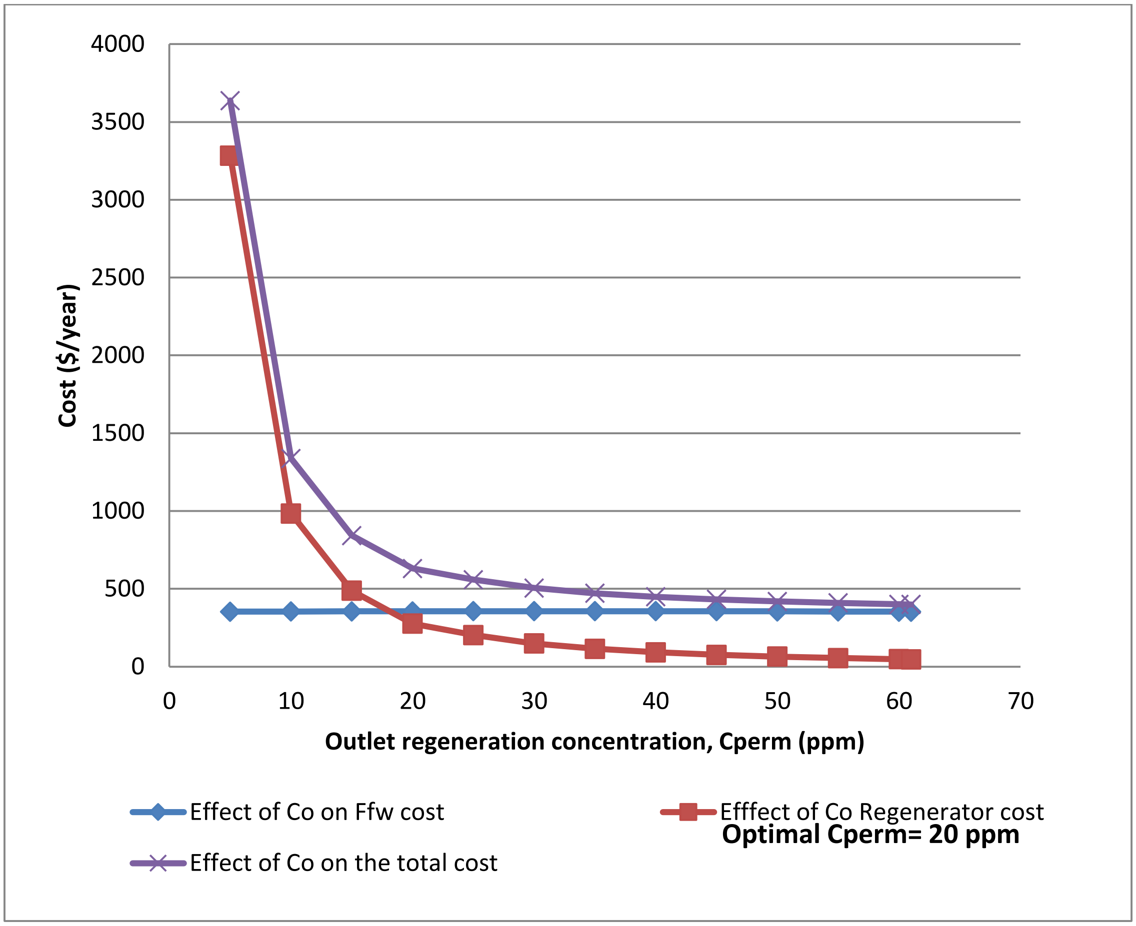


Figure 4.2.2 The cost function curves to locate an optimal C_{perm} for the fixed load problem

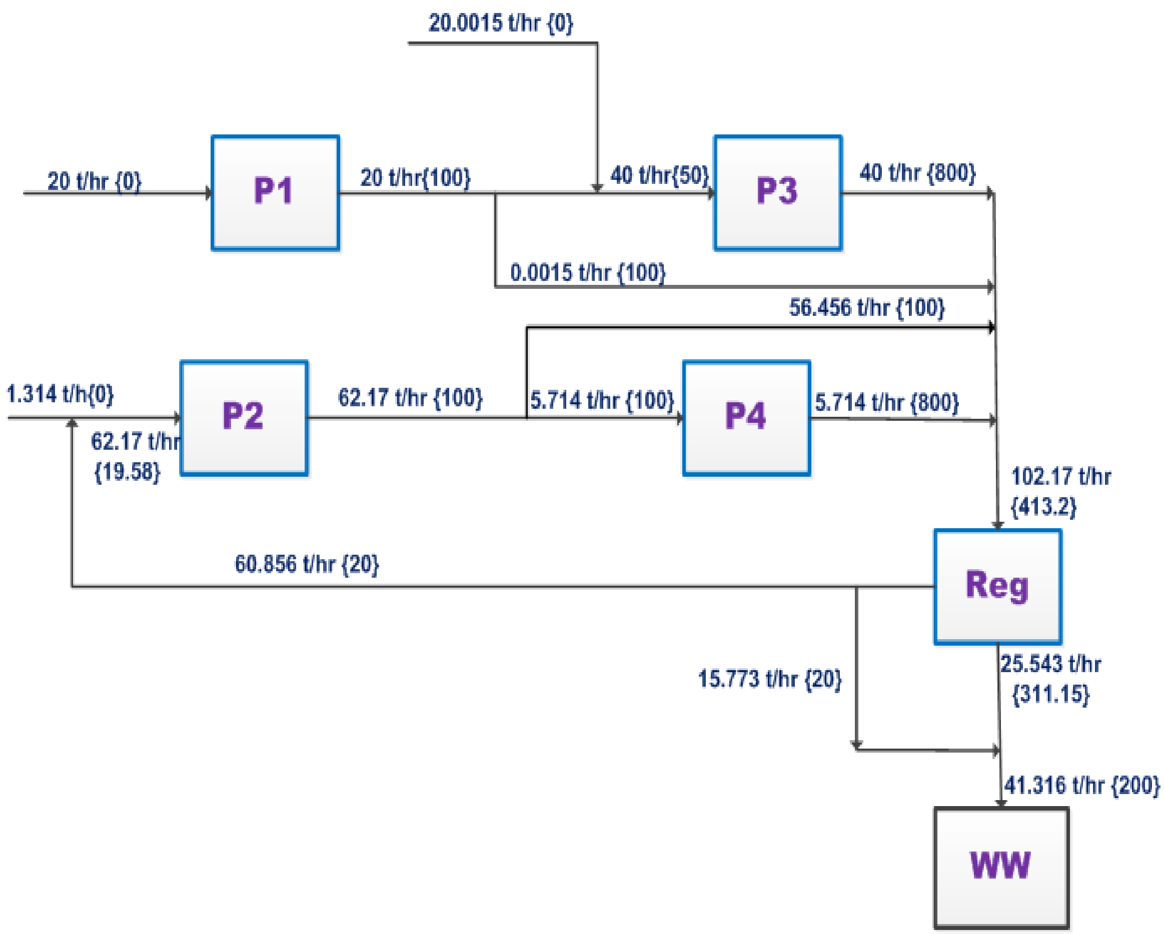


Figure 4.2.3 The optimal flowsheet design for the fixed load problem

The flowsheet design in Figure 4.2.3 is simpler with only 12 matches obtained upon the removal of the local recycles in the network. Moreover, the total water flowrate throughout the network was reduced from 340t/hr to 271.372t/hr, which is approximately 20% reduction of water flowing in the network. The results obtained in this work are compared to those achieved through Improved Problem Table (IPT) by Deng et al. (2016) as summarised in Table 4.2.3 below.

Table 4.2.3 Summary of the fixed load results compared with literature

	This Study	**Improved Problem Table** (Deng, et al., 2016)
Pre-regeneration concentration (C_{reg}, *in ppm*)	92.73	100
Post-regeneration concentration (C_{perm}, *in ppm*)	20	50; 150
Original freshwater requirement (t/hr)	170	170
Freshwater flowrate (t/hr)	41.32	72
Wastewater flowrate (t/hr)	41.32	72
Regenerated flowrate (t/hr)	76.63	144
% Freshwater savings	75.69	57.65
Freshwater cost (k$/yr)	335.31	619.2
Regeneration Cost (k$/yr)	306.91	65.02
Total Network Cost (k$/yr)	652.48	684.22

It can be concluded from Table 4.2.3 that the Improved CTA applied in this work is effective as the freshwater saving is 18.05% higher than the savings obtained with IPT. In addition, the reduction in cost is 4.64% higher for the Improved CTA. These savings are attained at optimal values of C_{reg}*=92.73 ppm*, C_{perm} *=20 ppm and RR=83.83*. On the contrary, the targets in IPT are obtained at estimated values of C_{reg}*=100 ppm* and C_{perm}*= 50 and 150 ppm*, with the former associated with the direct re-use and recycle pinch concentration. Moreover, there are 2 regenerators each with a fixed C_{perm} used to target the water network in IPT and the use of multiple regenerators proves to be unnecessary due to large regeneration cost incurred simultaneously with higher operational costs.

4.2.2 Application of the Improved CTA on a fixed flowrate problem

To illustrate the applicability of the Improved CTA on a Fixed Flowrate system, limiting data adapted from the work of Polley & Polley (2000) is used for this task. The limiting data is summarised in Table 4.2.4 below.

Table 4.2.4 Limiting data for the Fixed Flowrate problem (Polley & Polley, 2000)

Sources			Sinks		
	Flowrate (t/hr)	Maximum Outlet Concentration(ppm)		Flowrate (t/hr)	Maximum Inlet Concentration(ppm)
SR1	50	50	SK1	50	20
SR2	100	100	SK2	100	50
SR3	70	150	SK3	80	100
SR4	60	250	SK4	70	200
Freshwater	-	0	Wastewater	-	200

The data in Table 4.2.4 above is used to generate optimal flow and concentration targets using the Improved Composite Table Algorithm. The steps followed to obtain these results are summarised in Table 4.2.5 below. In this case, the fixed flowrate data is first converted to an equivalent fixed load data using procedures developed by Agrawal et al. (2006). Then the algorithm detailed in Figure 3.2.1 is applied. The difference between the fixed load problem illustrated in section 4.2.1 and the fixed flowrate problem discussed in this section is in terms of the flow loss from the water using system. As a result, the flow losses in this section are not zero but calculated to be 20t/hr. The major assumption applied to carry out the conversion of the fixed flowrate data to a fixed load type is that; initially the sinks are allowed to receive an infinite amount of load and this assumption is relaxed when the sources are introduced in the system to generate a Limiting Composite Curve (Agrawal & Shenoy, 2006).

Table 4.2.5 The Improved Composite Table Algorithm (CTA) at $C_{reg} \neq Cpr$

Process sources and sinks	Conc	Net flowrate	Net load (g/h)	Cumm Load (g/hr)	FW1	Ftu1,sys	C_{reg}
	0		0	0.00	0	**42.71**	
	20	0	0	0.00	0	0.00	
	50	50	1500	1500	30	-25.43	
	100	100	5000	6500	65	29.71	58.94
	150	**80**	4000	10500	70	**32.74**	92.55
	200	10	500	11000	55	14.04	63.06
	250	80	4000	15000	60	19.21	**96.68**
	300	20	1000	16000	53.33	11.58	76.20

SK2	SK2	SK3	SK4	SR1	SR2	SR3	SR4
100	100	80	70	50	100	70	60

F_{tu1}^{in} (t/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	F_{loss} (t/h)	C_{reg} (ppm)
55.46	42.71	32.74	0	96.68
F_{perm} **(t/h)**	C_{perm} **(ppm)**	F_{rej} **(t/h)**	C_{rej} **(ppm)**	$F_{tu1,e}^{prod}$ **(t/h)**
41.59	25.00	13.86	311.70	8.85
$F_{tu1,e}$ **(t/h)**	C_e^{mix} **(ppm)**	ΔC_e	**Error**	**%*RR***
22.71	200	0	1.00	80.61

It can be deduced from Table 4.2.5 above that the optimal flow targets of freshwater and wastewater were determined to be 42.71 t/hr and 22.71 t/hr, respectively. The targets are used to illustrate the feasibility of the Improved CTA technique, with the water supply line (WSL) completely below the limiting composite curve (LCC), as shown in Figure 4.2.4 below. The best cost for the water network was found at 25ppm and this is illustrated by Figure 4.2.5 below.

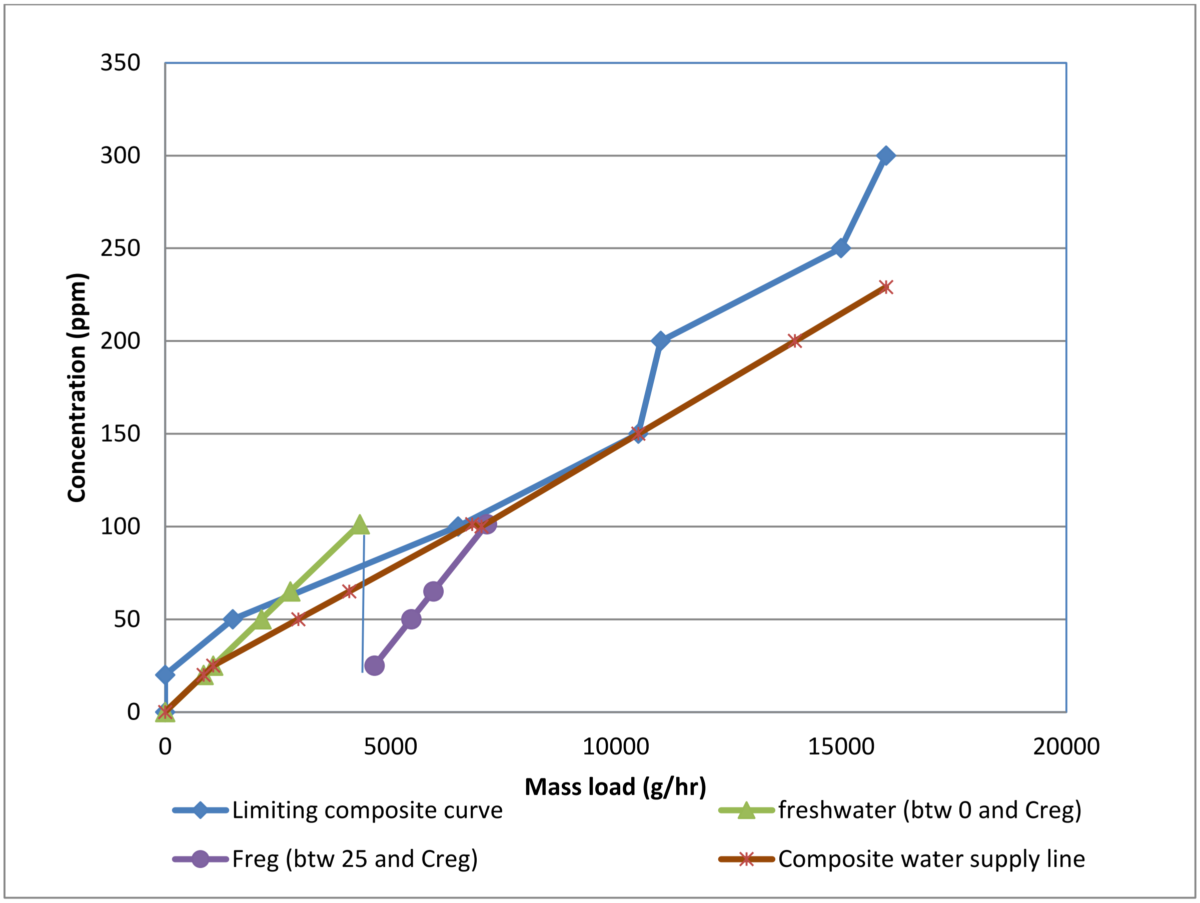


Figure 4.2.4 The graphs of Limiting Composite curve along with the Water Supply Line

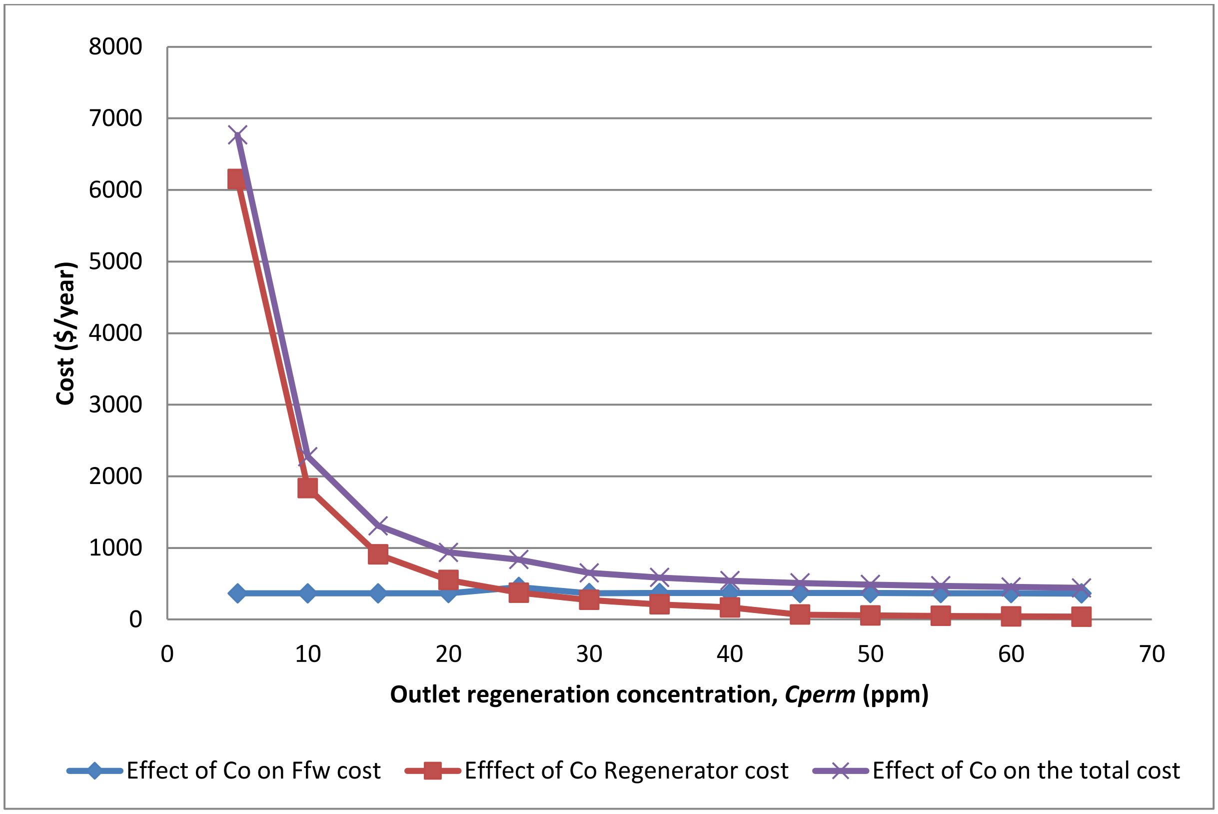


Figure 4.2.5 The cost function curves to locate an optimal C_{perm} for the fixed flowrate problem.

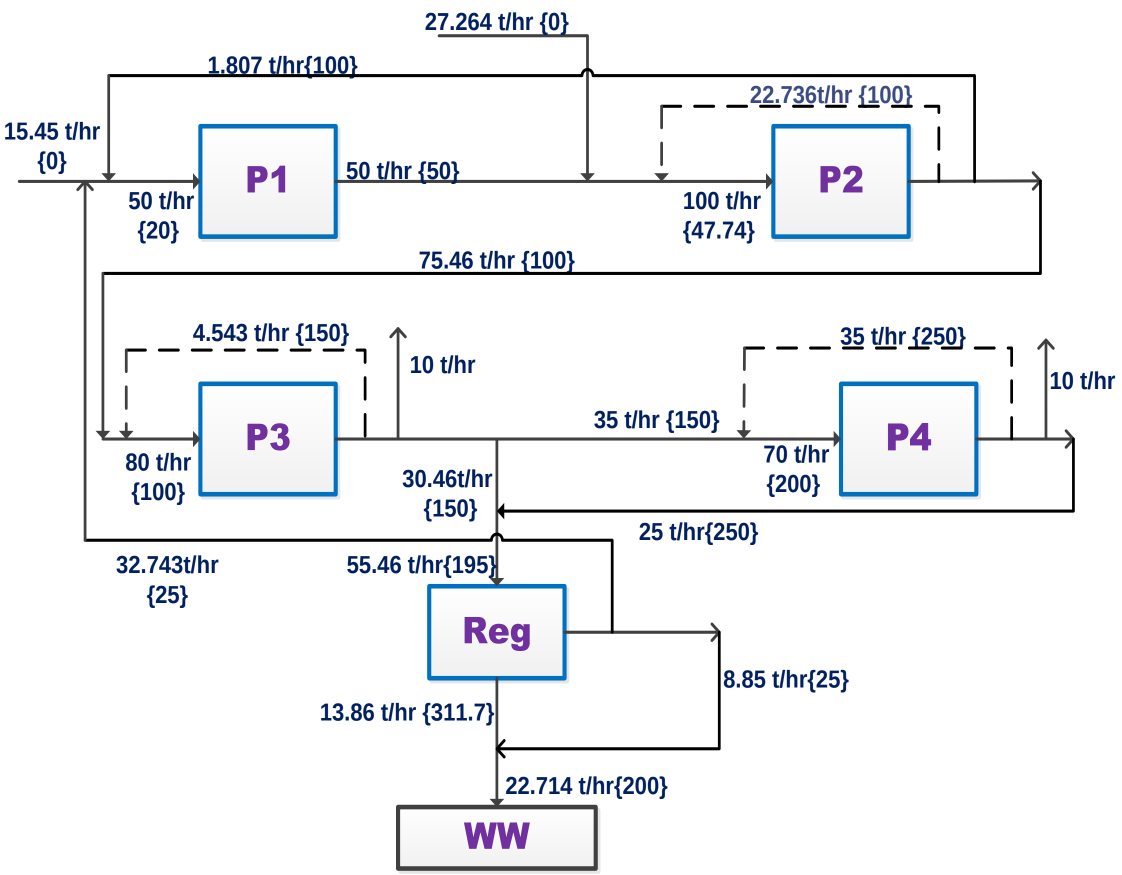


Figure 4.2.6 The optimal flowsheet design of the fixed flowrate problem

The optimal flowsheet design above was obtained using the nearest neighbour algorithm (NNA). The flowsheet design in Figure 4.2.6 is simpler with only 14 matches. Moreover, the total water flowrate throughout the network was reduced from 580t/hr to 278.17t/hr, which is approximately 53% reduction of water flowing in the network. The results for the fixed flowrate problem are summarised in Table 4.2.6, wherein they are compared with those obtained by Deng et al. (2016), who still applied the concepts of IPT.

Table 4.2.6 Summary of results for the fixed flowrate problem compared with literature

	This Study	**Improved Problem Table** (Deng, et al., 2016)
Pre-regeneration concentration (C_{reg})	96.63	100
Post-regeneration concentration (C_{perm})	25	50; 100;150
Original freshwater requirement (t/hr)	300	300
Freshwater flowrate (t/hr)	42.71	57.5
Wastewater flowrate (t/hr)	22.71	37.5
Regenerated flowrate (t/hr)	41.59	102.50
% Freshwater savings	85.76	80.83
Freshwater cost (k$/yr)	367.34	494.50
Regeneration Cost (k$/yr)	387.64	149.99
Total Network Cost (k$/yr)	754.98	644.49

It can be deduced from Table 4.2.6 above that there is about 6% freshwater savings achieved with the Improved CTA more than the IPT. However, the total network cost is cheaper with the application of IPT compared to the Improved CTA, although there was no systematic approach conducted in allocating the C_{reg} and C_{perm} values of the three (3) regenerators used in IPT. In the case of the improve CTA, the optimal values of C_{reg} and C_{perm} are 96.63 ppm and 25 ppm, respectively. These interdependent parameters were determined systematically using the proposed algorithm.

4.2.3 Application of the Improved CTA on a multiple contaminant problem

In the case of multiple contaminant problems, the water network targets and optimal designs are achieved first for the reference or key contaminant. The reference contaminant is the one that has its maximum inlet concentration equal to zero in the reference operation and obeys the monotonicity optimality condition (Savelski & Bagajewicz, 2000; Savelski & Bagajewicz, 2003). The optimality condition implies that the outlet concentration for every process must be greater than the concentration of the combined water streams fed to the processes from previous processes. The reference operation is the one that uses the cleanest water and this is operation 1, in reference to Table 4.2.7. The criterion followed for identifying this contaminant was developed by Calixto et al. (2015), and applied in this work along with the Improved CTA. The Nearest Neighbour Algorithm used to obtain optimal flowsheet designs is Improved to cater for a multiple contaminant problem. An illustrative fixed load example adapted from the work of Maria de Arruda et al. (2011), is used to demonstrate the applicability of reference contaminant approach on the Improved CTA. The process data, along with some calculated parameters necessary to identify the reference contaminant are summarised in Table 4.2.7 below.

Table 4.2.7 Process data for the multiple contaminants problem

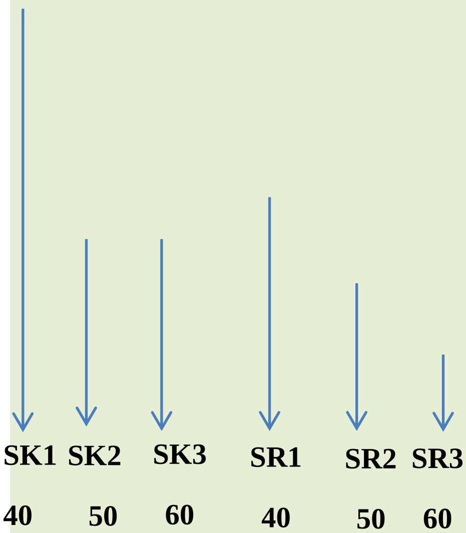
Processes	f **(t/hr)**	**Contaminants**	C_{in}^{max} **(ppm)**	C_{out}^{max} **(ppm)**	M **(kg/hr)**	$G_{u,c}^{w}$
P1	40	A	0	25	1	40
		B	0	37.50	1.50	40
P2	50	A	50	70	1	14.29
		B	50	70	1	14.29
P3	60	A	50	66.67	1	15
		B	50	66.67	1	15

In Table 4.2.7 above, the parameter $G_{u,c}^{w}$ determines which contaminant reaches its maximum inlet concentration first when freshwater is used and is calculated using Eq.4.13. The contaminant that has the highest $G_{u,c}^{w}$ value, along with the other criteria described above, is regarded as the reference contaminant. In this specific example, either contaminant A or B can be the reference contaminant as similar $G_{u,c}^{w}$ of 40 was calculated for each one of them. Therefore contaminant A was selected as the reference contaminant and used to calculate optimal flow targets and RR using the Improved CTA as illustrated in Table 4.2.8 below. The same flow targets used for the reference contaminant apply to the other contaminant B, however, different C_{reg} and RR are calculated for this contaminant with C_{e}^{mix} taken into account. The optimal flow targets and regenerator performance are summarised in Table 4.2.9 and compared with those obtained by Maria de Arruda et al. (2011), who incorporated 3 regenerators of fixed removal ratios in their water network.

$$G_{u,c}{}^{w} = \frac{\Delta M_{u,c}}{C_{u,c,out}{}^{max}} \tag{4.13}$$

Table 4.2.8 The Improved Composite Table Algorithm (CTA) at $\boldsymbol{C_{reg} \neq Cpr}$

Process Sources and Sinks	C_k (ppm)	$F_k{}^{net}$ (t/h)	$\Delta m_k{}^{net}$ (g/h)	$\Delta m_k{}^{cum}$ (g/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	C_{reg} (ppm)
	0		0	0	0	**39.16**	
	3.5	40	140	140	40	0	
	9.34	40	233.73	373.73	40	1.35	
	25	40	626.27	1000	40	0.98	
	50	0	0	1000	20	-20.60	
	66.67	110	1833.70	2833.7	42.50	3.53	7.75
	70	60	199.80	3033.5	43.34	**4.40**	**9.34**
	100	0	0	3033.5	30.34	-9.14	-17.63



$F_{tu1}{}^{in}$ (t/h)	F_{fw} (t/h)	$F_{TU1,sys}$ (t/h)	F_{loss} (t/h)	C_{reg} (ppm)
43.56	39.16	4.40	0	A:9.3433 B:9.3428
F_{perm} (t/h)	C_{perm} (ppm)	F_{rej} (t/h)	C_{rej} (ppm)	$F_{tu1,e}{}^{prod}$ (t/h)
32.67	3.5	10.89	26.87	28.27
$F_{tu1,e}$ (t/h)	$C_e{}^{mix}$ (ppm)	ΔC_e	**Error**	**%RR**
39.6	10	0	1.00	A:71.905 B:71.903

Presented in Table 4.2.9 below are summary of results for the multiple contaminant problem compared with literature to emphasize the efficiency of the proposed technique.

Table 4.2.9 Summary of results for the multiple contaminants problem compared with literature

	This study	**Water Surplus Diagram,** (Maria de Arruda, et al., 2011)
Regenerator type	Partitioning	Single Pass
No. of regenerators	1	3
Regenerator Performance (%*RR*)	A: 71.905	R1 → A: 95
	B: 71.903	R2 → A: 80; B: 90
		R3 → A: 95
Regenerated flowrate (*t/hr*)	32.67	60.429
Freshwater flowrate (*t/hr*)	39.16 (↓ 2.1%)	40

In Table 4.2.9 above, almost the same freshwater target is achieved in both techniques (only 2.1% reduction with the Improved CTA). However, in the case of Improved CTA, it is obtained at optimal *RR* calculated for each contaminant in a single regenerator. These results are depicted in Table 4.2.9 above, where the *RR* of contaminant A and B were calculated to be 71.9% and 65.24%, respectively. The flowsheet design of the water network was achieved through expanding the NNA to handle multiple contaminants, with conservation of the fixed mass load to be removed. These results are shown in Table 4.2.10 below.

Table 4.2.10 Network design of the fixed load system for the multiple contaminants problem

			Fsk (t/hr)	~~40.000~~ 39.155	43.556	~~50~~ 20.002	~~60~~ 26.670	39.155
			Csk B (ppm)	0	7.5530	~~50~~ 37.500	~~50~~ 35.300	~~10.000~~ 8.0100
			Csk A (ppm)	0	9.3430	~~50~~ 25.000	~~50~~ 26.323	10.000
Fsr (t/hr)	Csr B (ppm)	Csr A (ppm)	SR vs SK	SK1	Freg,in	SK3	SK2	WW
39.155	0	0	Fso	**39,155**				
4.4003	3.5000	3.5000	Freg,sys				4.4000	
~~40.000~~ 39.155	37.500	25.000	SR1	~~0.84500~~ LR		20.002	19.153	
10.889	19.711	26.873	Frej					10.889
~~50.000~~ 20.002	66.670	66.670	SR3		**16.885**	~~29.998~~ LR	3.1170	
~~60.000~~ 26.67	70.000	70.000	SR2		26.670		~~33.330~~ LR	
28.266	3.5000	3.5000	Freg,e					28.266

In reference to Table 4.2.10 above, the NNA is applied such that each demand (SK1 to SK3) is satisfied by the nearest neighbor sources. This can be illustrated with demand SK1 at 0 ppm for both contaminant concentrations of A and B, where the requirements are initially satisfied by both the freshwater source and source SR1. However, the source SR1 is later removed as it is the local recycle and this is illustrated by the red line crossing over its flowrate requirement of 0.845 t/hr. Note that in the application of the NNA, preference is placed on maximising flowrates in the local recycles of the individual operations. This is because the local recycles can be removed without violating the fixed mass load of the operations. This approach also results in sinks requirements being met at concentrations below their threshold values. This can be illustrated with sink (SK3), which before the removal of the local recycle (LR) stream, required 50 t/hr of water and the maximum inlet concentration for both the contaminants was 50 ppm. Then after the removal of the local recycle, the flowrate requirement reduced to 20 t/hr and the inlet concentrations of contaminant A and B were calculated to be 25 ppm and 37.5 ppm, respectively. The flowsheet designed using the results from the NNA, is depicted in Figure 4.2.7. The mass load observation around operations or processes are calculated using Eq.4.14 and illustrated in

Table 4.2.11 below, where *LR* refers to the local recycle. This observation of load is ensured to avoid violations that may yield infeasibilities in the water network and the results.

$$\Delta M = f \times \{C_{out}{}^{max} - C_{in}{}^{max}\} \qquad (4.14)$$

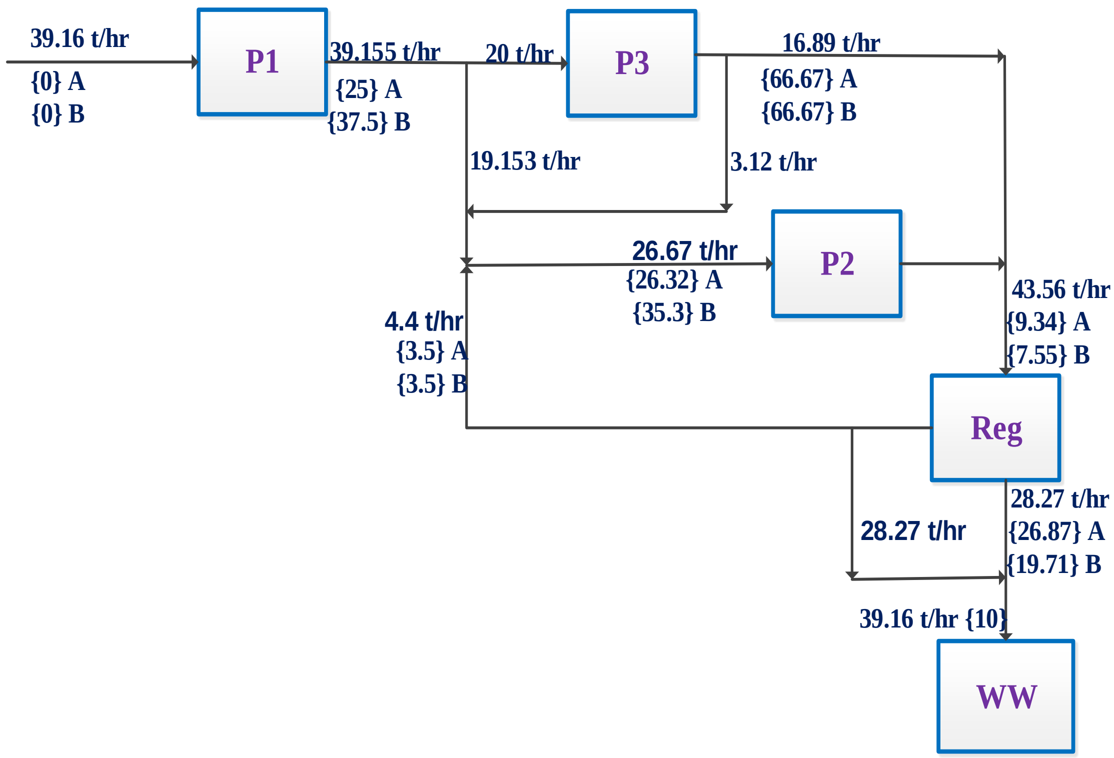


Figure 4.2.7 The optimal flowsheet design for a multiple contaminant problem

The flowsheet design in Figure 4.2.7 is simpler with only 9 matches obtained upon the removal of the local recycles in the network. Moreover, the total water flowrate throughout the network was reduced from 300t/hr to 168.54t/hr, which is a 43.8% reduction of water flowing in the network.

Table 4.2.11 Fixed load data for feasibility checks on each process for each contaminant

Contaminant A in Processes	Load without *LR*	Load with *LR*	Contaminant B in Processes	Load without *LR*	Load with *LR*
P1	1	1	**P1**	1.5	1.5
P2	1	1	**P2**	1	1
P3	1	1	**P3**	1	1

4.2.4 Application of the Improved CTA on an industrial case study of a fixed flowrate problem

The industrial case study used for illustration in this work is adapted from the work of Klemes (2013). The case study involves minimisation of water in a Water Fabrication Plant. This is a semi-conductor plant, where a large amount of freshwater is consumed to produce ultrapure water (UPW) for use in the fabrication section (FAB). This is in addition to water consumption in the utility section i.e. general cleaning; cooling tower makeup and scrubber feed water. The plant consists of four UPW consuming processes in the FAB, i.e. wet processing section (Wet), Lithography, and combined chemical and mechanical processing (CMP) and miscellaneous operations (MisOp). Note that the UPW fed to these processes may be viewed as process feedstock while those for general cleaning purposes are treated as utility water. Upon usage, some processes produce wastewater streams. This is water network synthesis problem of a single contaminant. The limiting data for this case study is provided in Table 4.2.12 below.

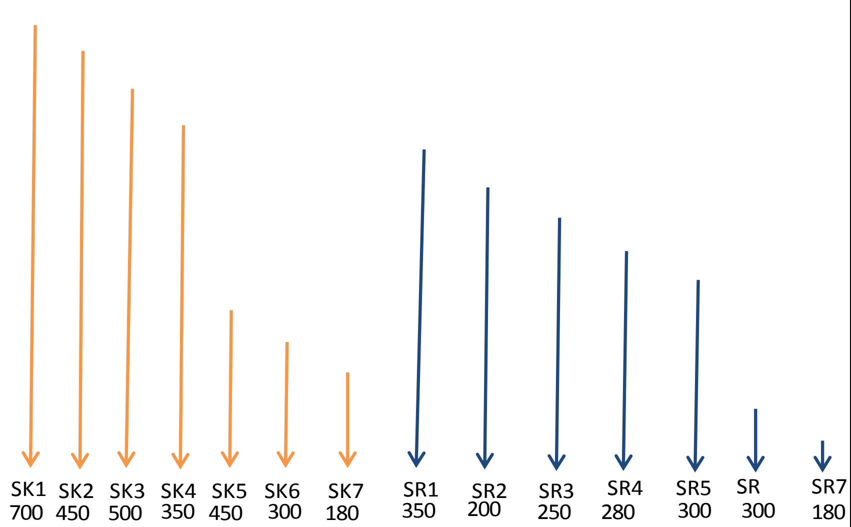
Table 4.2.12 Limiting data for the industrial case study: Water Fabrication Plant

Sources			Sinks		
	Flowrate (t/hr)	Maximum Outlet Concentration(ppm)		Flowrate (t/hr)	Maximum Inlet Concentration(ppm)
Wet l	250	1	Wet 1	500	0.143
Wet ll	200	0.5	Lithography	450	0.125
Lithography	350	0.33	CMP	700	0.1
CMP l	300	10	MisOp	350	0.2
Other	280	2	Cooling Tower	450	50
Cleaning	180	500	Scrubber	300	100
Scrubber	300	500	Cleaning	200	125
Freshwater	-	0	Wastewater	-	3

The data in Table 4.2.12 above is used to generate optimal flow and concentration targets using the Improved Composite Table Algorithm. The steps followed to obtain these results are summarised in Table 4.2.13 below.

Table 4.2.13 The Improved Composite Table Algorithm (CTA) at $\boldsymbol{C_{reg}} \neq \boldsymbol{C}pr$

Process sources and sinks



Conc	Net flowrate	Net load (g/h)	Cumm Load	FW1	Ftu1,sys	Creg
0,00		0,00	0,00	0,00	**1220,34**	0,08
0,10	0,00	0,00	0,00	0,00	0,00	
0,13	700,00	17,50	17,50	140,00	-3000,95	-0,04
0,14	1150,00	20,70	38,20	267,13	-2163,63	-0,04
0,20	1650,00	94,05	132,25	661,25	-931,82	-0,02
0,33	2000,00	260,00	392,25	1188,64	-41,85	0,05
0,50	1650,00	280,50	672,75	1345,50	149,00	0,10
1,00	1450,00	725,00	1397,75	1397,75	192,84	0,19
2,00	1200,00	1200,00	2597,75	1298,88	81,81	0,17
10,00	920,00	7360,00	9957,75	995,78	-226,38	-1,53
50,00	620,00	24800,00	34757,75	695,16	-526,03	-18,52
100,00	1070,00	53500,00	88257,75	882,58	-338,03	-23,84
125,00	1370,00	34250,00	122507,75	980,06	-240,43	-21,19
200,00	1550,00	116250,00	238757,75	1193,79	-26,56	-3,70
500,00	1250,00	375000,00	613757,75	1227,52	7,18	2,60
600,00	1070,00	107000,00	720757,75	1201,26	-19,08	-8,04

F_{tu1}^{in} **(t/h)**	F_{fw} **(t/h)**	$F_{TU1,sys}$ **(t/h)**	F_{loss} **(t/h)**	C_{reg} **(ppm)**
1413,18	1220,34	192,84	0	2,598
F_{perm} **(t/h)**	C_{perm} **(ppm)**	F_{rej} **(t/h)**	C_{rej} **(ppm)**	$F_{tu1,e}^{prod}$ **(t/h)**
1059,88	0,08	353,29	10,15	867,05
$F_{tu1,e}$ **(t/h)**	C_e^{mix} **(ppm)**	ΔC_e	**Error**	**%*RR***
1220,34	3,00	0	1,00	97,69

Upon applying the Improved CTA in Table 4.2.13 above, optimal flow target of 1220.34t/hr was obtained for both freshwater and wastewater and pre-regeneration concentration of 2.598 ppm. To illustrate the feasibility of these targets, a Limiting Composite Curve was generated along with the water supply line, from which the latter curve lies completely below the former. This implies that there is no violation in terms of the mass load to be removed and these findings are illustrated in Figure 4.2.8 below. In reference to Figure 4.2.9 below, the best cost was found at a Co or C_{perm} value of 0.08ppm, from which an optimal removal ratio of 97.691% was obtained.

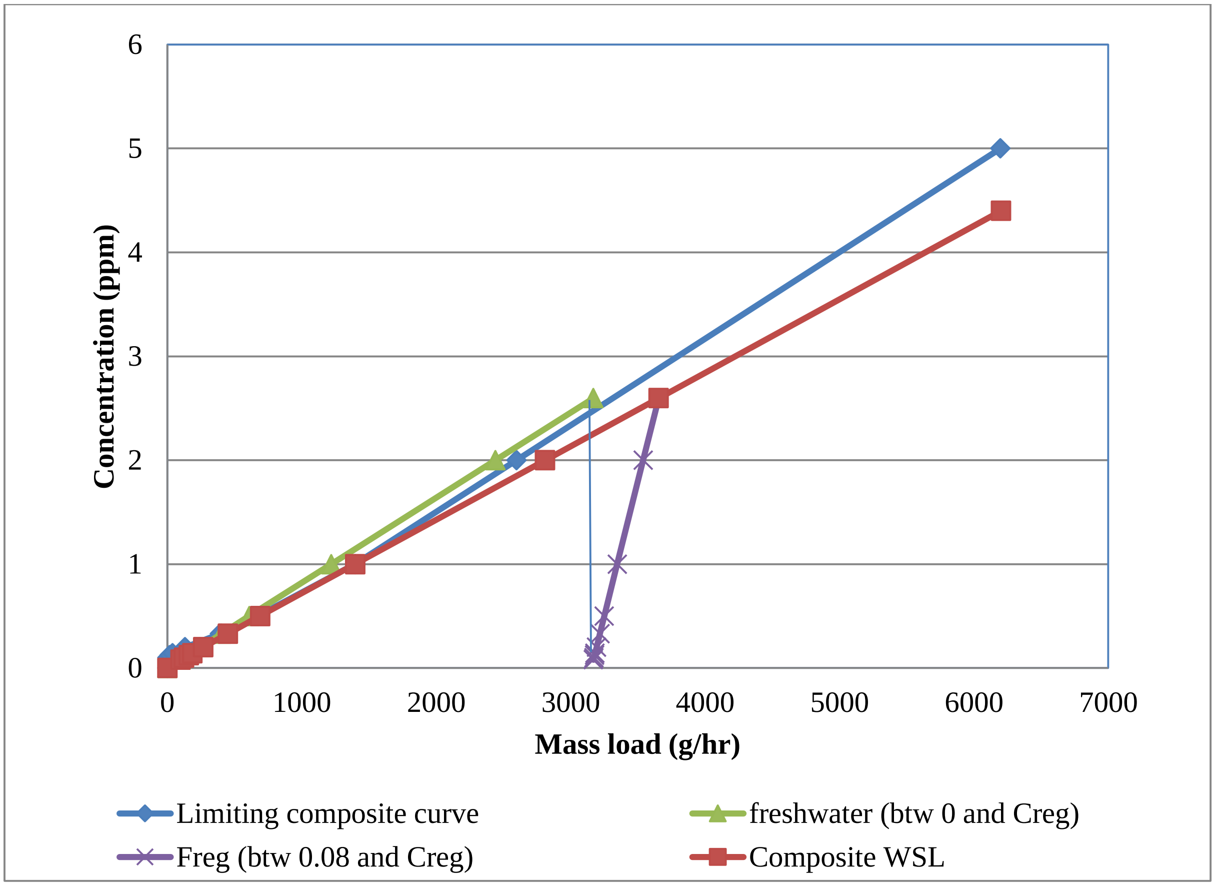


Figure 4.2.8 The graphs of Limiting Composite curve along with the Water Supply Line

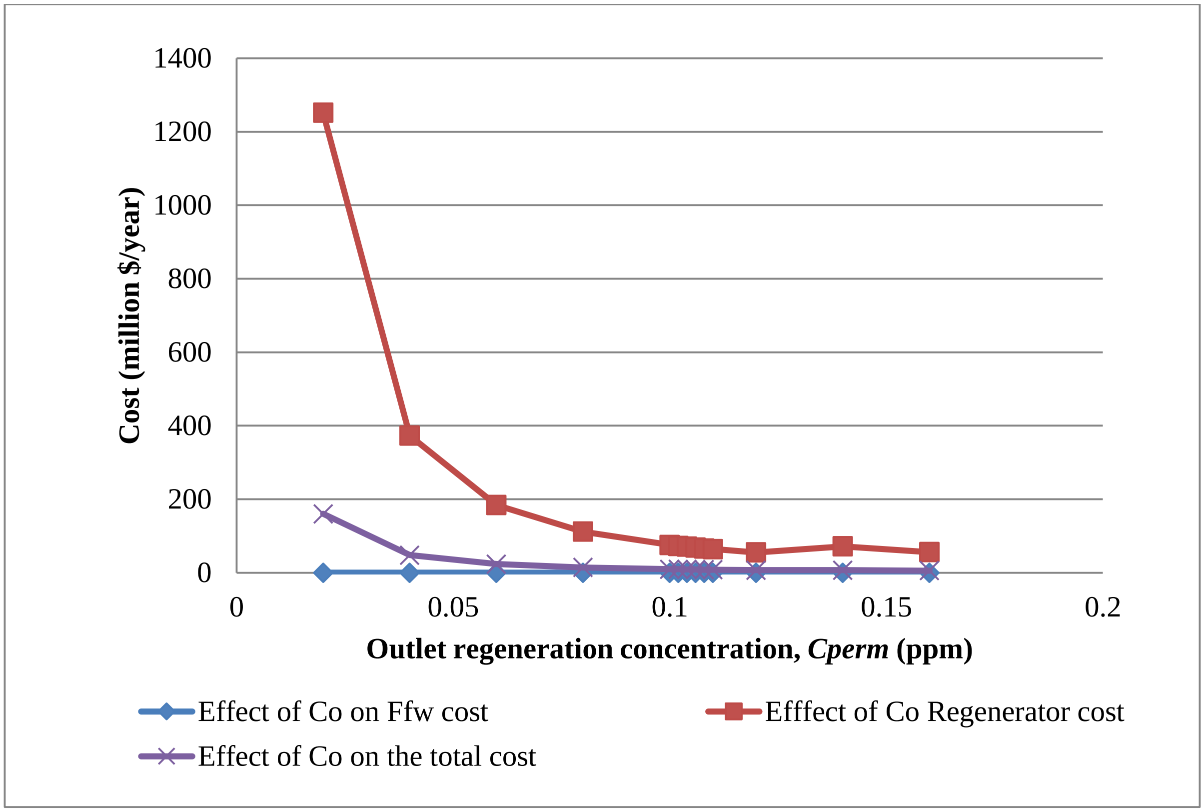


Figure 4.2.9 The cost function curves to locate an optimal C_{perm} for the industrial case study

4.3 Integrated framework of graphical and mathematical techniques

Due to the complexity of mathematical problems, optimization of such problems is usually subjected to issues of uncertainty. Optimization under uncertainty refers to cases where the model to be solved involves uncertain data or estimated parameters and this is known as stochastic programming or stochastic optimization problems (Diwekar, 2003). There are deterministic mathematical programmes that can help one develop effective or interpretable solutions of complex algebraic formulations. In this work, an algebraic mathematical programme called GAMS was used to deal with uncertainty in the mathematical optimization. The sub-solvers used include BARON, which was used to solve MINLP, CPLEX for solving MIP and Minos for solving NLP.

There are three cases analysed in this section to illustrate the benefits of a hybrid system as proposed in this work. The illustrative example of the fixed load problem (Table 4.2.1) is used in the first case. The analysis in case 1 is carried out through three stages. In the first stage, the results obtained from the Improved CTA are validated using mathematical modelling. In this case, the regenerators are modelled as black box. In the second stage, detailed regeneration design of a reverse osmosis unit (RO) is incorporated within the water network to account for accurate regeneration cost. In this case, there is no integration between the graphical and mathematical techniques. Instead, the effect of the variable removal ratio on the model convergence is analysed. The last stage is the hybrid framework, wherein the results obtained from the Improved CTA are used to initialize the mathematical model. In this stage, the *RR* obtained from graphical targeting (CTA) is set as a parameter in the mathematical formulation. The second scenario is a fixed load problem for multiple contaminant system. In case 2, the use of the Improved CTA to preprocess mathematical modelling is compared with a literature example that also uses the water surplus diagram (WSD) as a preprocessing step. The third case exploit the benefits of the hybrid framework over the independent use of mathematical modelling to solve the water network, and this is illustrated using the industrial case study of the water fabrication plant.

4.3.1 Results for case 1: fixed load problem

The results for the fixed load problem adapted from Table 4.2.1 in section 4.2.1 are summarised below.

Table 4.3.1 Summary of results for the mathematical modelling (fixed load problem)

	Stage 1	**Stage 2**	**Stage 3**
	Blackbox model	Variable RR	Fixed RR
Freshwater flowrate (t/hr)	39.6	226.8	212.4
Wastewater flowrate (t/hr)	39.6	226.8	212.4
Cost of Reg (k$/year)	80.45	5.4	7.69
Total Cost (k$/year)	428.77	3624.93	3627.97
Removal Ratio	0.884	0.864	0.884
CPU time (hrs)	0.0072	35.71	**5.54**

The results obtained for stage 1 in Table 4.3.1 above show that there is 5.17% increase in the *RR* obtained using mathematical model compared to the *RR* obtained with the Improved CTA (calculated at 0.84). However this difference is small considering the simplifying assumptions associated with graphical targeting techniques. In order to minimize the total network cost in stage 1, the model favours the use of less freshwater but more regenerated water, and this is concluded from the high regeneration cost obtained for this stage. However, a linear cost function is used for the blackbox regenerator in this stage; which the model identified as the cheaper option. On the other hand, stage 2 incorporates a detailed regeneration design which takes into account the true regeneration cost and therefore accurate account of the total water network cost. In this case, the model favours the use of more freshwater than the regenerated water to minimize the overall network cost. This observation is concluded from the lower regeneration cost and higher freshwater requirement obtained for stage 2 compared to stage 1.

The same observation applies to stage 3 as it also includes a detailed design of the regenerator. Moreover, stage 2 incurs larger computational time (about 36 hours) when the system is allowed to determine an optimal RR. However, when an integrated system is analysed in stage 3, the computational time reduces significantly to approximately 6 hours. These results prove the effectiveness of the use of graphical targeting techniques to initialize or preprocess mathematical modelling. This is because there is 85% reduction in the CPU time of the hybrid or integrated system at an expense of only 2.26% error in the RR specified. Note that the detailed regeneration design conducted using mathematical modelling takes into account the true regeneration costs and therefore accurate cost representation to the total water network. As a result, the mathematical component of this integrated framework makes it applicable to real life industrial case study.

Table 4.3.2 The model characteristics for the fixed load problem

	Variable *RR*	**Fixed *RR* (Hybrid system)**
Number of constraints	147	147
Number of continuous variables	121	120
Number of discrete variables	41	41

It is important to note that the initialization contributes to the reduction of variables in the mathematical formulation and this lead to faster model convergence. This investigation is motivated by models developed in literature which were reported to be computationally intensive (Buabeng-Baidoo & Majozi, 2015; Abass & Majozi, 2016) . As a result, the model characteristics for the fixed load problem are reported for both scenarios of variable removal ratio and fixed removal ratio (for the hybrid system). These results are depicted in Table 4.3.2 above. It can be derived from Table 4.3.2 that the hybrid system has one less variable (120) compared to the scenario of variable *RR* (121). Although the difference in the number of variables is very small, it contributes significantly to the model computational time as validated by the CPU values in Table 4.3.1 above. The optimal flowsheet design of the mathematical model with all interconnections between the sources, sinks and the regeneration unit is presented in Figure 4.3.1 below. Note that the values depicted on the diagram are flowrates in tons per hour.

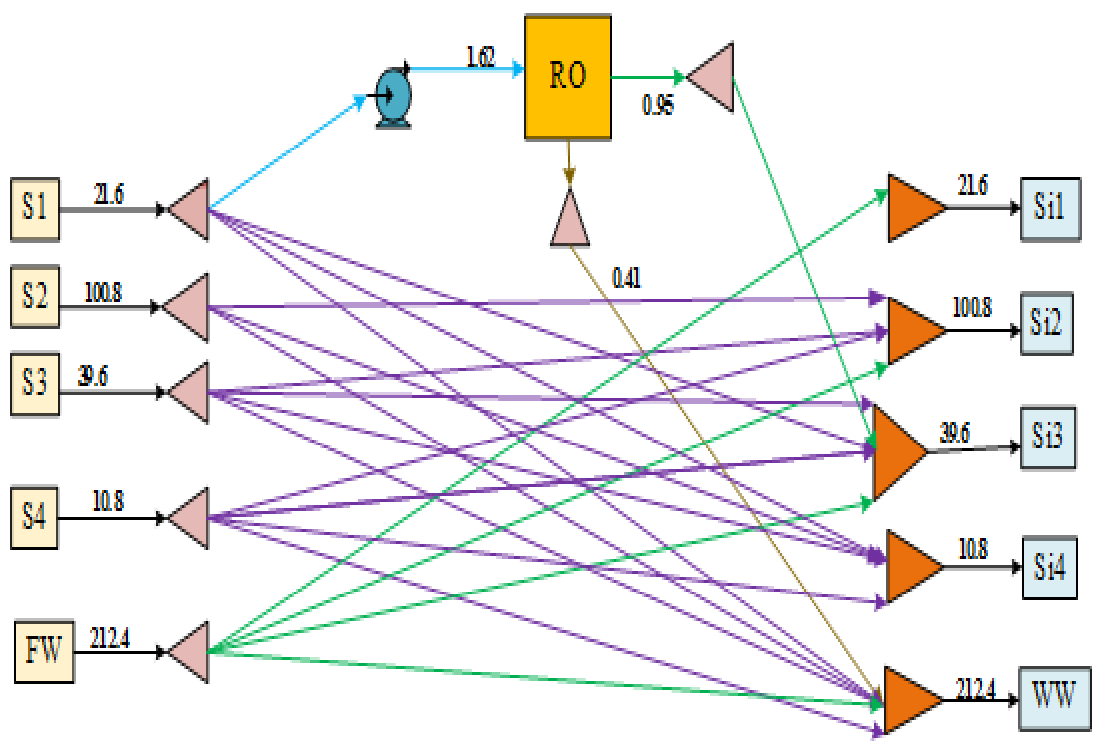


Figure 4.3.1 Optimal water network flowsheet for case 1 (hybrid framework)

4.3.2 Results for case 2: multiple contaminant problem

Presented in Table 4.3.3 below are the results for integrated framework, wherein the systematic framework proposed in this work is compared to results published in literature. In this case, the proposed frameworks integrate pinch based techniques (CTA and WSD) with mathematical formulations to reduce model complexity.

Table 4.3.3 Results for the integrated framework (multiple contaminant problem)

	This work	**WSD with GAMS (Maria de Arruda, et al., 2011)**
Objective	Minimize cost	Minimize cost
Freshwater flowrate (t/hr)	352.8	40
Wastewater flowrate (t/hr)	352.8	40
Regenerated water flow (t/hr)	1.273	65.01

In order to illustrate the advantages of the integrated framework in Table 4.3.3 above, the process data used was adapted from the work of Maria de Arruda et al. (2011). The integrated framework developed by these authors is compared to the systematic framework proposed in this work. Their technique involved integrating the water surplus diagram (WSD) with GAMS to solve the water network. As depicted in Table 4.3.3 above, the integration proposed in this work favors the use of more freshwater (at 352.8 t/hr) over regenerated water (at 1.273 t/hr) to solve the water network as opposed to the other technique. These results are expected because the integration of the WSD with GAMS considers the regenerator as a black box and consequently finds the option of regenerated water cheaper than freshwater. However, this is impractical for industrial purposes, thus limiting the technique.

4.3.3 Results for case 3: industrial case study

Presented in Table 4.3.4 below are the mathematical results for the industrial case study. In this case, the water network of variable *RR* is compared with that of the fixed *RR* (the hybrid framework).

Table 4.3.4 Mathematical results for the industrial case study

	Variable RR	**Fixed RR**
Freshwater flowrate (t/hr)	27324	27255.6
Wastewater flowrate (t/hr)	26251.2	26384.4
Cost of Reg (k$/year)	4.36	2.29
Total Cost (k$/year)	470516	426655
Removal Ratio	0.981	0.977
CPU time (minutes)	26.10	**0.0821**

The results obtained for the variable *RR* in Table 4.3.4 above show that the model determined an optimal *RR* of 0.981, which is only 0.41% higher than the *RR* determined by the Improved CTA (at 0.977). This difference in accuracy of results is very small considering the benefits brought by the hybrid framework. One major benefit is the reduction in CPU time for the case of integrated CTA and mathematical modelling, wherein Table 4.3.4 reveals that computational time of approximately 5 seconds were incurred to solve the water network. This is a reduction of 99.69% from the 26.1 minutes computational time utilization for solving the water network with variable *RR*. It is noteworthy that the compromise in accuracy of results for the proposed hybrid framework is insignificant compared to the large savings in computational time and model complexity. The optimal flowsheet design of the integrated water and regeneration network is illustrated in Figure 4.3.2 below.

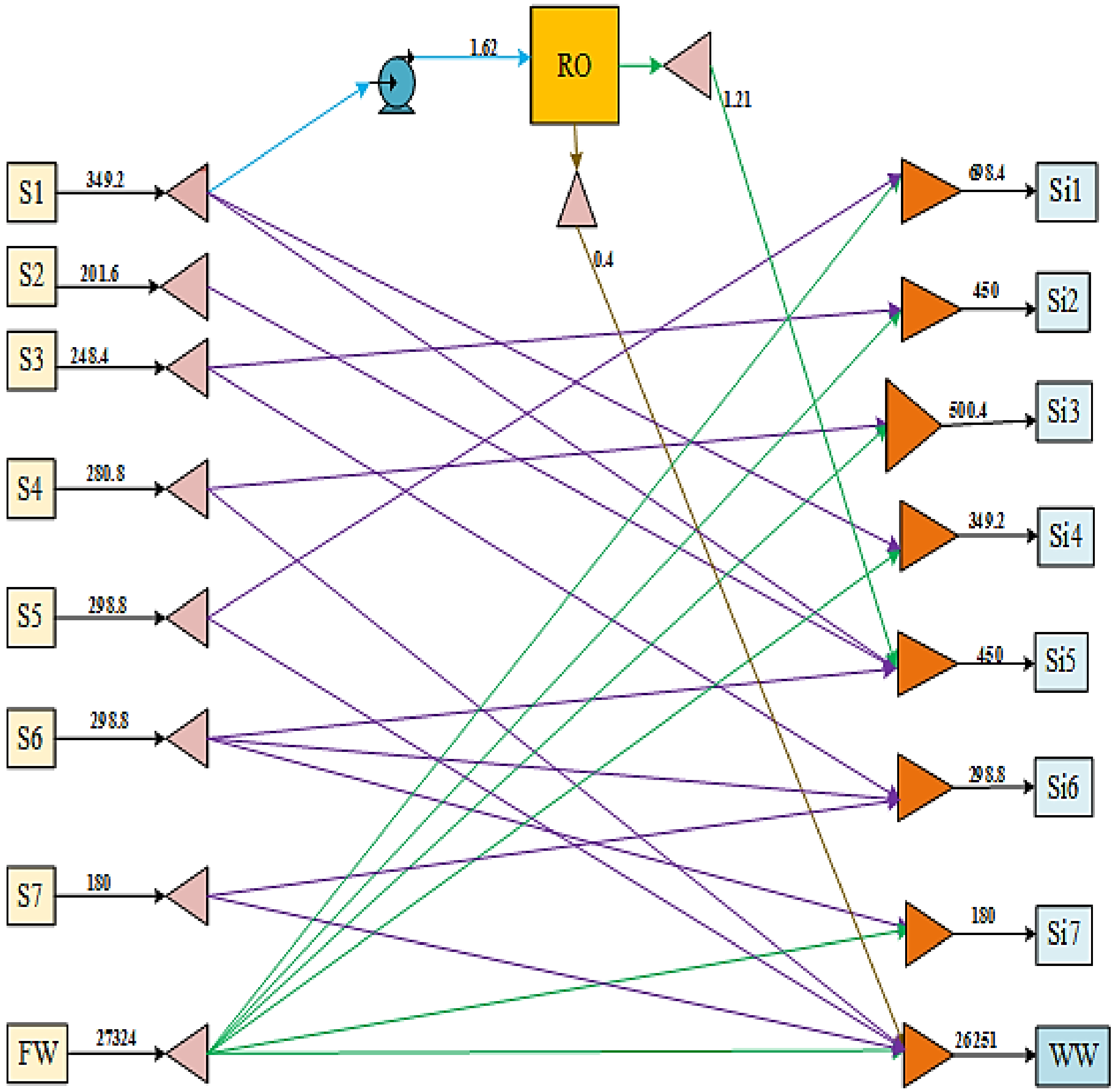


Figure 4.3.2 Optimal water network flowsheet for case 3 (at *RR*= 0.981)

4.4 Conclusions

This work explores the benefits of integrating graphical techniques with mathematical modelling in the water network optimisation, by using the Improved CTA as a preprocessing technique for mathematical formulation. The proposed integrated framework was successfully applied on fixed load water network, multiple contaminants problem and an industrial case study. The results obtained show the benefit of this systematic framework as there is evidence of 85% reduction in CPU time in one of the problem considered (the fixed load network), implying faster model convergence. The contributions offered by this study include the determination of an optimal post-regeneration concentration and consequently optimal RR using graphical framework, for a partitioning type regenerator. Moreover, the approach minimizes the freshwater requirement in the network, the wastewater production and the overall network cost in all different illustrative examples.

4.5 References

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CHAPTER 5

Chapter 5 Recommendations and Considerations

5.1 Introduction

This chapter aims to offer scope for future work in the field of water network synthesis. The methods proposed to improve the solution procedure of water networks optimization techniques are based on the shortcomings of the work presented in this dissertation. There are recommendations provided in this chapter for further development of the proposed Improved CTA. Then the challenges for industrial membrane applications are discussed with the objective of addressing some efficient pre-treatment routes which can be adopted. Lastly, due to the high computational expense associated with the optimization of water networks embedded with detailed regeneration units, preprocessing strategies are discussed to help reduce model complexities and consequently computational time.

5.2 Recommendations for the Improved CTA

It is noteworthy that the proposed Improved CTA has been successfully applied as a pre-processing technique to problems of fixed flowrate, fixed load, multiple contaminants water networks and to an industrial case study. Despite all these achievements and contributions, the following aspects are recommended for future research:

a) The Improved CTA has been successfully developed for total water networks (which incorporated direct water reuse/recycle, regeneration reuse and effluent treatment). The type of regenerator used is a partitioning type regenerator, wherein the freshwater flowrate is not necessarily equal to the regenerated water flowrate (this is the case with total regeneration for single pass type regenerators) due to occurrences of mass load infeasibilities (Parand, et al., 2013). In the case of partitioning type regenerator, the regenerated water flowrate (permeate stream) is often lower than the freshwater feed. Moreover, the freshwater flowrate can be lower in the case of regeneration recycle. As a result, for further reduction in the freshwater requirement, the Improved CTA can be further improved to incorporate regeneration-recycle in the total water network.

b) In order to optimise the proposed Improved CTA, cost optimization was conducted under the assumption of unit fixed costs. It is presumed that varying the unit cost can lead to a totally different water network; therefore it is recommended that cost sensitivity analysis is conducted in future works.

c) Most industries invest in wastewater pre-treatment to minimize regeneration cost as pre-treatment reduces the load to be removed by the treatment facilities. Therefore, the proposed technique can be improved to cater for wastewater pre-treatment.

d) The proposed algorithm is developed for water networks with a single regeneration unit; therefore future work can expand this technique to work on multiple regenerators' water network. Moreover, this technique can be expanded to cater for different threshold problems; i.e. those which require freshwater feed with no waste disposal, those which have no freshwater feed but have wastewater productions and lastly, special cases which require neither freshwater or wastewater discharges.

e) In this work, the algorithm for the Improved CTA is terminated once the possibility of removing infeasibilities in the water network is unavailable. This situation occurs when a specific C_{perm} yields negative flowrates in the table and consequently infeasible solutions even after ΔC_e is set to zero. Future work can explore the possibilities of removing infeasible pockets by incorporating pseudosinks and pseudosources as suggested by Parand et al. (2016).

5.3 Membrane technologies

Membrane technologies in the field of wastewater minimization have been widely used. However, the hydrophobicity nature of some of these membranes, reduce their permeability. This undesirable characteristic results from extreme pH of the wastewater, from which the membranes become susceptible to non-specific adsorption of hydrophobic contaminants in water and consequently give rise to fouling issues (Judd & Jefferson, 2003). In this work, it assumed that fouling of the membranes is negligible as there is chemical pre-treatment of the wastewater before regeneration in the reverse osmosis unit. In addition to pre-treatment, fouling issues can further be alleviated by developing membranes with hydrophilic surfaces. According to Judd & Jefferson (2003), this can be achieved through chemical oxidation and the use of organic chemical reactions or grafting from which an additional organic layer can be added onto the polymer surface of the membrane. Note that oxidative chemicals such as chromic/ nitric acid help functionalize the surface so that it is hydrophilic and this is done through converting alkenes and esters of the surface to hydroxyl and carboxylate groups (Judd & Jefferson, 2003).

a) In light of the above background, it is therefore recommended that industrial applications of membrane technologies adopt some of these surface modification routes in order to increase the robustness of their membranes.
b) There is no evidence of regeneration recycle in the optimal flowsheets of the work presented in this dissertation, regardless of the fact that this is allowed or considered in the model formulation. It possible that upon minimizing the objective function, the model found such a connection costly and therefore discarded it. However, some industrial applications of wastewater treatment have local recycles of regeneration-recycle. Although such practice further minimizes the amount of freshwater requirement, it leads to contaminant accumulation in the system (Chang & Li, 2005). It is therefore recommended that further investigations are conducted to evaluate the trade of between the benefits of significant freshwater reductions and the challenges caused by contaminant accumulation due to local recycles (in particular membrane fouling issues). It is possible that it may be worthwhile to forbid local recycles in the model formulation at a penalty of a minor increase in the freshwater cost.

5.4 Methods to reduce computational time

The issues of computational time are prevalent under cases where the model to be solved has high number of discrete variables, binary variables and bilinear terms which yield a nonlinear non-convex MINLP model formulation. This is the case with the resultant models solved in Chapter 4, wherein high computational times incurred in the case of variable removal ratio. However, upon fixing the removal ratio in the integrated system, the computational time reduced significantly due to reduction in model complexity. In this dissertation, graphical targeting tools

(Improved CTA) is successfully applied as preprocessing step for mathematical modelling to help reduce the computational time. There were approximately reductions of i.e. 85% CPU time at a low % error of 2.26 for the fixed flowrate problem. This integration or hybrid framework is also supported by some work of researchers, which showed potential to enhance the formulation and reduce the model size (Ng, et al., 2009; Alva-Argáez, et al., 2007; Alva-Argáez, et al., 1998). Although this work revealed that pinch based have the potential to increase convergence of mathematical models, the following are a few of the mathematical algorithms which can achieve the same outcome:

a) It is recommended that linearization of some of the bilinear terms in the model is conducted and this can be achieved through the use of either McCormick's over and under estimators for the product of two continuous terms or the Glover transformations for the product of an integer and continuous variables.
b) Moreover, the use of MILP-based piecewise-affine relaxation schemes can be used to handle bilinearities (Khor, et al., 2014).
c) An RLT method proposed by Quesada and Grossmann (1995)**,** which first solve the linear model and use the results as the starting point and lower bound for the nonlinear model is recommended. This approach help with model convergence and contribute to achievement of near global or global optimum solutions and shorter computational times., thus reducing computational time an

5.5 Conclusions

In summary, there are challenges associated with the use of mathematical programming for water network synthesis. These challenges include convergence issues which arise from the nonconvexity and nonlinearity of the models formulated. As a result, preprocessing strategies are proposed in order to aid reduce computational time of these models. Moreover, the success and limitations of the Improved CTA that offers scope for future work are discussed. In overall, the recommendations made in this chapter are aimed at making improvements on the proposed integrated framework of the mathematical modelling and graphical insights.

5.6 References

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CHAPTER 6

Chapter 6 Conclusions

This work explores the benefits of integrating graphical techniques with mathematical modelling for water network synthesis. The aim of investigating an integrated or hybrid approach was to reduce both model complexity and large computational time incurred during mathematical optimisation of the integrated water and regeneration network. As a result, a pinch based technique known as the Composite Table Algorithm (CTA) was modified and both the minimum water flow targets and optimal regenerator performance obtained from it where used to initialize the formulated mathematical model. In essence, this systematic framework uses the proposed Improved CTA to pre-process the complex MINLP model formulation, that which incorporates a detailed regenerator design of a reverse osmosis (RO) unit.

To demonstrate the applicability of this approach, it was applied to two literature examples of fixed flowrate and fixed load problem. It was further applied to an industrial case study of a Water Fabrication Plant and also used to solve a multiple contaminant water network of a fixed load problem. The modelling platform used was GAMS/BARON. The results obtained highlight the practicality and benefits of this systematic framework as there is evidence of 85% reduction in CPU time in one of the problem considered, implying faster convergence for the proposed framework. The contributions offered by this study include the determination of an optimal post-regeneration concentration and consequently optimal removal ratio using graphical framework, for a partitioning type regenerator.

Furthermore, there is great benefit in allowing the removal ratio in the model to be a variable. This gave the model more flexibility and impacted significantly on the cost and structure of the network. Although such flexibility reportedly results in large computational time, that specific shortcoming is eliminated in this work through the use of the Improved CTA to determine an optimal removal ratio prior the detailed design.

Lastly, the systematic approach developed in this work successfully minimizes the freshwater requirement in the network, the wastewater production and the overall network cost. Since a single regenerator was used in the proposed framework, this offers scope for future work to incorporate multiple regenerators and/ integration of others types of regenerators such as ultrafiltration units, nanofiltration units and electrodialysis. Furthermore, the insights and rigour obtained from this systematic framework offers future research directions to explore the potential of other pinch based graphical or algebraic techniques for mathematical pre-processing.