Numerical and experimental investigation of chlorine demand and decay in water distribution systems.

Numerical and experimental investigation of chlorine demand and decay in water distribution systems

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DECLARATION

I hereby declare that the dissertation submitted for the degree of MASTER OF ENGINEERING IN CHEMICAL ENGINEERING at the Tshwane University of Technology is my own original work and has not previously been submitted to any other institution of higher education. I further declare that all sources cited or quoted are indicated and acknowledged through a comprehensive list of references.

Donald Maphanga

DEDICATION

The dissertation work is dedicated to my family. I would like to give special thanks to my forever-loving mom, Dudu Maphanga, and granny, Thakgudi Maphanga for their continuous encouragement and support throughout this journey. My brothers, Andrew, and Simon Maphanga have always been on my side and always cheered me up during this journey. To my loving son, Lwazi Thamsanqa Maphanga, I thank you for giving me a purpose to work and study extra hard. I would like to also thank the almighty GOD for making this journey possible.

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LIST OF PUBLICATIONS

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ABSTRACT

It is crucial to control the chlorine residual within the portable water distribution network/system to ensure the delivery of safe water to end-users as per regulatory requirements. In this study COMSOL Multiphysics and EPANET softwares were employed concurrently to respectively develop solute transport and water quality regression-based mathematical and computational models for first order and second order chlorine decay to simulate the impact of reaction mechanisms, chlorine initial dose, bulk decay coefficient, pH, chlorine demand, breakpoint chlorination, and chlorine concentration profiles at different distances within the water distribution system supplied by the Vaalkop Water Treatment Plant (WTP). The developed computational models were validated by laboratory experimental results and literature reviews as part of quality assurance. Experimental results were simulated using a pipe length of 1 meter for solute transport and 100 kilometers for the water quality model. The chlorine dosages ranged from 2.5 mg/L to 20 mg/L, with a reaction time spanning from 0 to 4419 minutes. The chlorine demand for lower dosages, ranging from 2.5 mg/L to 5 mg/L, was high, with 98% of the chlorine dose being consumed within 15 minutes of reaction time.

Elevated chlorine dosages, between 10 mg/L and 20 mg/L, exhibited a chlorine demand of less than 60% of the initial chlorine dose within 15 minutes, and caused formation of Trihalomethanes disinfection byproducts after 15 minutes of reaction time. The bulk decay rate for the mathematical models displayed exponential decay, ranging from 0.3 (mg/L.min) to 0.0001 (mg/L.min), for chlorine dosages ranging from 2.5 mg/L to 20 mg/L. The regression-based second order models achieved a determination of coefficient (R2) of 98% with respect to chlorine dose, while the first

order models achieved 86%. The bulk decay rate for the simulated models ranged from 0.035 (mg/L.hr.m) to 0.000021 (mg/L.hr.m) for dosages ranging from 2.5 mg/L to 20 mg/L in the solute transport models, and 0.3 (kg/hr) to 0.00021 (kg/hr) for the water quality models. Rapid chlorine decay, with 98% of the chlorine dose being observed within 10 kilometers for the water quality models and 0.1 meters for the solute transport models, was observed for lower chlorine dosages below 5 mg/L. Chlorine dosages exceeding 10 mg/L satisfied the chlorine demand of the system and maintained chlorine residual levels above 1.3 mg/L at the exit points for both solute transport (1 meter) and water quality models (100 kilometers).

The optimal chlorine dosage for the system was determined to be 6.30 mg/L, which would maintain chlorine residual within ±0.5 mg/L at the point of use without the formation of disinfection byproducts. However, the upper limit for chlorine supply within the system was set at 5 mg/L that would require the installation of chlorine boosters within a 5-kilometer radius of the system. First order chlorine decay models are contingent upon the chlorine reaction time, whereas second-order chlorine decay models are reliant on the initial chlorine dose. The parameters of the second order chlorine decay model are linearly associated with the chlorine dose. The reaction of chlorine in aqueous solutions is pH-dependent, and chlorine decay does not affect water pH. The results of this study demonstrated the applicability of the developed solute transport and water quality models for determining accurate chlorine dosing requirements to reduce costs and ensure compliance with regulatory frameworks.

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NOTATIONS

$Cl(t)$	Chlorine at time t (mg/L)
Cl_0	Initial chlorine dosage (mg/L)
t	Reaction contact time (minutes)
k	First order bulk reaction rate coefficient (1/min)
k_1	First order fast chlorine decay rate (1/min)
k_2	First order slow chlorine decay rate (1/min)
k_w	Wall chlorine decay rate coefficient(1/min)
k_b	The bulk chlorine decay rate (1/min)
K	The overall chlorine decay rate (1/min)
R	The model parameter for second order
u	The bulk chlorine decay rate for second order model (1/min)
n	The reaction order model
x	The parallel first order model parameter
C^*	The concentration for limited first order model (mg/L)
k_f	The bulk decay rate for two reactant first order model (1/min)
$C_{Cl,dose}$	The initial chlorine dose (mg/L
C_i	The concentration of specie I (mg/L)
x	The pipe length (m)
u_i	The fluid velocity (m/s)
r	The reaction rate (mg/L/min)
K_0	The regression based bulk decay rate (L/min/mg)

β	The regression-based decay rate coefficient (1/min)
J_{cl}	The chlorine diffusivity mass flux (mol/m^2.s)
R_{cl}	The chlorine reaction rate (mol/m^3.s)
D	Diffusion coefficient (m^2/s)
p	The fluid density (kg/m^3)
P	The fluid pressure (N/m^2)
F	The volume force vector (N/m^3)
τ	The viscous stress tensor (N/m^2)
V_i	The average velocity in pipe I (m/s)

ABBREVIATIONS AND ACRONYMS

DWDNS	Drinking water distribution network systems
SMP	Soluble microbial products
UV	Ultraviolet light
NOM	Natural organic matters
THMs	Trihalomethanes
HAAS	Halo acetic acids
HANS	Halo aceto nitriles
S/V	Surface to volume ratio
DOC	Dissolved organic carbon
EEM	Excitation emission matrix
DOM	Dissolved organic matter
DBPs	Disinfection by-products
2R	Two reactant model
TOC	Total organic carbon
RANs	Reynolds-averaged Navier-stokes
3D	Three dimensions
SR	Single reactant model
EPANET	Environmental protection agency network
EPANET-MSX	Environmental protection agency network multispecies
EPANET-RTX	Environmental protection agency network real-time extension
ODEs	Ordinary differential equations
FCRS	Fast chlorine reactive substances
SCRS	Slow chlorine reactive substances
SRA	Slow reducing agent
TCD	Total chlorine demand
ICD	Instantaneous chlorine demand
LCD	Lasting chlorine demand
PFOM	Parallel First order model
QCRS	Quantitative chlorine reactive substances

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND AND MOTIVATION

Drinking water is essential for daily household usage, industrial applications and to be utilized by the community in various ways. Water is impure when there are active contaminants that poses a threat to the public health. The direct or indirect contaminated water establish a pipeline of transporting chronic illnesses from the environment to human and animals if consumed without prior purification (Nono et al., 2018). The death toll of human beings is estimated to be 829 000 death per year due to water-borne illnesses worldwide (WHO., 2011). Water treatment plants are designed to ensure the production of saf water that is within the set quality standards as recommended by the World health Organization (WHO) and South African National Standards (SANS) (Mamba et al., 2008, Monteiro et al., 2020, WHO., 2011) . The water distribution network systems (WDNS) transport the treated water to the designated community for consumption. Water quality when leaving the water treatment plant should remain constant throughout the water distribution network to the point of use or the consumer's tap, however this is not always the case hence the post disinfection process is applied to control the deterioration of water quality in water distribution systems through the use of water disinfectants (Sun et al., 2016).

Post or tertiary water disinfectants are dosed in the final water to destroy the cells of active natural organic matters and other inorganic matters present in the bulk water and pipe walls (Zhao et al., 2018). Excessive disinfectant dosage destroys all

the pathogens that are present in the final water and establish a residual that is harmful for human consumption, while the dosing of insufficient disinfectant in the final water gets depleted instantaneously through the biofilm that is attached on the pipe surfaces and accelerates the regrowth of micro-organisms and pathogens that are harmful for human consumption (Li et al., 2019, Marta and Silva, 2016). It is critical to control the disinfectant residual to ensure that the regrowth of micro-organisms is prohibited and the concentration at the point of use is safe for consumption (Monteiro et al., 2017).

For numerous decades, chlorine has been found to be the most efficient and cost effective disinfectant dosed during the tertiary water disinfection process and is used by various water utilities in the whole world (Nono et al., 2018). Chlorine is highly reactive in water and depends on the water pH (Abokifa et al., 2019). The reaction of chlorine with chlorine reactive substances (CRS) involves the combination of natural organic matters such as ammonia and many more, the inorganic matters includes and not limited to; iron(Fe), manganese(Mn) , and other biological matters that are found in the bulk water and the biofilm that is attached on the pipe walls (Kelly et al., 2014, Kowalska et al., 2018). The CRS are dependent on the water quality and the chlorine demand of the system (Abokifa et al., 2016).

Excessive chlorine decay surpass the chlorine demand of the system and establish the disinfection by-products formed during the oxidation of organic matters known as Trihalomethanes (THMs) that are harmful for consumption and less chlorine does not satisfy the chlorine demand of the system thus compromising the purpose of water disinfection (Gomes et al., 2016). Also, the properties of the distribution network that comprise the hydraulic velocity, pipeline materials and biofilms along

with physicochemical and microbial properties of water play a huge role in the efficacy of chlorine (Hu et al., 2016).

It is regulated to ensure that the chlorine concentration at the point of use is at 0.5 mg/L as the World Health organization stipulates (Mamba et al., 2008, WHO., 2011). Maintaining the chlorine residual requires monitoring of the water quality and chlorine demand of the system throughout the WDNS (Van der Walt et al., 2021). The monitoring of the chlorine residual levels in the WDNS requires to take water samples at time intervals along the pipe lines of the system and this is challenge since well the pipes are embedded under the surface, thus make it difficult to access the sampling points (Monteiro et al., 2017, Nono et al., 2018).

Bulk chlorine decay studies are performed in laboratory environment to determine the chlorine decay rate in the water samples and the wall decay studies are predicted by adding the bulk decay rate with the depletion rate of chlorine in the pipes summing to the overall chlorine decay rate (Monteiro et al., 2015a, Morrison et al., 2022). It is quite tedious and time consuming to run series of experiments every often to determine the bulk decay rate since it is dependent on water quality that varies with season and source (Marta and Silva, 2016). Mathematical models were developed and improved to assist in curbing the experimental work load, however these models are limited in graphical visualizations (Tiruneh et al., 2019). Chlorine decay models follow three traditional orders which are: zero order, first order and second order (Wang et al., 2019). This reaction orders were found to be weak and the introduction of integrated and improved mathematical orders were established, thus the complexity of chlorine decay expands due to the dependence

on water quality and omitting some modelling parameters to suit the studied variables (Clark, 2015).

Water quality model simulator (EPANET) software has been used world-wide since 1994 as the finite element method to study the depletion of chlorine decay in water distribution networks (Fisher I, 2017). EPANET software is limited to studying only the traditional mathematical models that were found to be less effective (Cong et al., 2017). Solute transport model simulator (COMSOL Multiphysics) is used to simulate the effect of fluid flow dynamics and chlorine transport in water distribution systems (Hoai and Hoang, 2017). COMSOL Multiphysics software is equipped with the capability to perform both traditional and integrated chlorine decay models, however the solute transport modeler is suitable for discrete variables, time dependent and take longer period of simulation times when performing complex chlorine decay models (Goodarzi et al., 2020).

It is clear that numerous factors such as water composition, properties of the pipelines, and organic compounds within the water distribution network play a huge role in the level of residual chlorine within the distribution network. However, sustainability in terms of the laboratory experiments and mathematical models in terms of chlorine consumption and decay is scarce in literature hence creating an avenue for research. This study focused on the assessment of chlorine decay using experimental studies and then develop numerical and computational models for first order and second order regression-based chlorine decay that could be used to simulate the effect of reaction mechanism, chlorine initial dose with chlorine demand, bulk decay coefficient, pH and concentration profiles with distance in the distribution system. This research evaluated chlorine demand and decay in attempts

to improving the water distribution system and reduce the imbalance of chlorine residuals in the water distribution system and networks. Specifically, COMSOL Multiphysics coupled with EPANET softwares were used in parallel to develop the finite element analysis (FEA) and water quality models for both first and second order chlorine decay. The developed solute transport and water quality models were validated by laboratory experimental and literature data as part of quality assurance.

1.2 PROBLEM STATEMENT

The process of optimizing chlorine residual concentrations in water distribution networks through experiments is laborious, time-consuming and expensive. In this study computational models for solute transport and water quality were developed. However, the developed computational and numerical models need to tested/validated with experimental results for accurate predictions of chlorine dosing requirements in water distribution network.

1.3. RESEARCH AIM AND OBJECTIVES

1.3.1 Aim

The overall aim of this study was to evaluate and optimize the chlorine demand and decay of a water distribution system using experimental and numerical methods.

1.3.2. Objectives

To achieve the overall aim of this research, the following specific objectives were developed:

I. To determine the chlorine demand and decay profiles of the system using experimental studies and assays, specifically the effect of concentration, pH and time.

II. To develop first and second order regression-based chlorine decay models using COMSOL Multiphysics and EPANET softwares and simulate the effect of chlorine dose concentration on chemical chlorine profiles, bulk chlorine decay rates and model parametric sensitivity.

III. To evaluate optimum chlorine dose and validate the chlorine decay models in the distribution systems using experimental and available literature data.

1.4. SIGNIFICANCE OF THE STUDY

The study aims to contribute to the understanding of chlorine decay mechanisms and the development of accurate kinetic models. These insights will shed light on factors influencing chlorine decay, enabling optimization of water treatment processes for effective disinfection, and maintaining residual chlorine levels. Gaining a better understanding of chlorine decay mechanisms could enhance the ability to accurately model the behavior of chlorine residuals in water distribution systems, particularly in scenarios involving water mixing (Monteiro et al., 2020). Additionally, this study aims to investigate the relationship between chlorine dose and the formation of disinfection by-products (DBPs) during the slow and lasting chlorine decay phase. By examining this relationship, the study seeks to identify effective strategies for managing and mitigating the formation of DBPs (Lemus Peres and Rodriguez Susa, 2017). This study attempts to fill a gap in research by investigating the correlation between water quality models and solute transport models using a regression-based chlorine decay model. By integrating numerical and simulated models, the study seeks to understand the impact of bulk decay coefficients on chlorine decay over distance. The developed models were rigorously validated using experimental and existing literature data. Additionally, the study

would highlight the importance of break-point chlorination, chlorine demand, and optimal chlorine dosage techniques.

1. 5. STRUCTURE OF THE DISSERTATION

This dissertation is configured as follows:

Chapter One (1): Introduction – This chapter provides the necessary background information related to the focus of the study. The chapter discusses the challenges that exist in the specific area of study and outline the objectives formulated to address these challenges. Lastly the significance of the study is discussed.

Chapter Two (2): Literature review – The literature review chapter provides a comprehensive overview of the theoretical background concerning chlorine decay in the context of drinking water treatment and distribution networks. This chapter reviews laboratory studies, numerical approaches, and computational fluid dynamics (CFD) models that have been employed to investigate and understand the process of chlorine decay.

Chapter Three (3): Materials and Methods- In this chapter, the laboratory experiments, developed computational and numerical models for the study are presented. The chapter emphasizes the research focus on the analytical techniques, numerical methods, configurations of the computational fluid dynamic (CFD) models, and quality control approaches used to investigate and model chlorine decay.

Chapter Four (4): Results and Discussions- This chapter presents a comprehensive discussion of the results obtained from the application of the numerical and analytical methods highlighted in the methodology section. The chapter discusses the results related to chlorine decay models as guided by the objectives of the study. The quality and validity of the modeled results are also reported.

Chapter Five (5): Conclusions and Recommendations- In the final section of this dissertation, insightful conclusions are drawn based on the key results of the chlorine decay models, in relation to the objectives of the study. The conclusions will summarize the main outcomes and contributions of the research, highlighting the significance of the findings in addressing the research objectives.

CHAPTER 2

LITERATURE REVIEW

2.1 RAW WATER

Unprocessed or raw water refers to water that is not treated and contains high amounts of minerals, bacteria, pathogens, cations (K^+, Na^+, Ca^+, Mg^+, Fe^{2+}, and more), anions(Cl^-, NO_3^-, SO_4^{2-}, and more) (Vingerhoeds et al., 2016). The raw water can be found as a product of precipitated water from rainfall, water stored under the landscape, unfiltered water wells and from water flowing sources such as rivers and lakes (Wang et al., 2019). The contaminants that are found in the raw water causes undesirable water pH, taste, odor, turbidity and therefore, renders the water unsafe for consumption (Krishna and Sathasivan, 2020). Consumption of drinking water that is microbiologically and chemically polluted has been causing severe health damage to consumers such as infants, young children, elderly or unwell people or those who are immune compromised (Simoes and Simoes, 2013). Raw water is treated in portable or drinking water treatment plant to critically control the water quality and produce safe water for consumers (Masindi and Dunker, 2016).

2.2 DRINKING WATER TREATMENT PROCESS

The processes of treating drinking water involve the combination of physical, chemical, and biological methods to improve the water quality for consumers (Abokifa et al., 2016). A water treatment plant is equipped with units that perform pre-disinfection, coagulation, flocculation, sedimentation, filtration, and post-disinfection. The pre-disinfection phase is when the dosing of chlorine or other disinfectant is added into the feed water to remove the pathogens, bacteria,

microbes and other chlorine reactive contaminants present in the water (De Boer and Gonazalez-Rodriguez, 2022).

A coagulant in a form of chemical is then added to attract the negatively and positively charged colloids that are dissolved and suspended in the water (Lemus Peres and Rodriguez Susa, 2017). The added chemical remove the dissolved organic and inorganic matters (Li et al., 2019). The flocculation phase employs the slow stirring of the treated water to allow the inter-particle collision and form large flogs that could be physically filtered. In the sedimentation process, the dense suspended particles or flocks are allowed to settle through the gravitational force.

The settled particles are removed by passing them into a filtration medium (Slow Sand Filters) at a rate of 4-24 $min^{-1}/10\ dm^2$. A post disinfection process is the last step in the water treatment plant to ensure that 99.9 % of the inorganic and organic matters that managed to survive during the purification phases are destroyed and inactivated completely (Liu et al., 2014, Monteiro et al., 2015a, Xu et al., 2018). Chlorine is widely used in the post disinfection stages to react with all the pathogens present in the final water, however the chlorine residual is not effectively controlled due to the interchanging of bulk and wall chlorine demand (Van der Walt et al., 2021).

2.3 FUNCTIONALITIES OF DRINKING WATER TREATMENT PROCESS

To safeguard the health of end-users, drinking water should be of a specified quality to ensure that it is safe for consumption without posing an intermediate or long-term harm to the consumers (Tiruneh et al., 2019). The drinking water treatmentprocesses are designed to effectively prevent the deterioration of final water quality (Van der Walt et al., 2021). The inter-link of the water treatment plant units are designed to ensure that if pathogens managed to survive the first stages

of the treatment process therefore they should be eliminated in the next stage until the final step (Sun et al., 2016, Wang et al., 2019).

2.4 FINAL WATER AND CHALLENGES

The physical, chemical, and biological processes that occurs in the water treatment plants dictate the water quality that would reach the consumer's tap (Marta and Silva, 2016). Drinking water treatment and post chlorination processes does not destroy all biomass present in raw water sufficiently and micro-organisms in final water still persists in lower concentrations to further consume the chlorine residual(Saidan et al., 2017, Srivastava and Bhargava, 2015).

Some of the contributing factors that affects the final water quality integrity are biofilm growth (Srivastava and Bhargava, 2015), nitrification (Lemus Peres and Rodriguez Susa, 2017) , leaching substances from network materials, internal pipe corrosion (WHO., 2011), scale formation on the pipe surfaces (Zhang et al., 2017) and the formation of disinfectant by-products that further consume the chlorine residual (WHO, 2011). Scales formation on the drinking water conduits are being caused by the solid materials deposits during post-treatment, upstream corrosion, and deposits (Zhang et al., 2017).

The effect of low flow of water, low chlorine residual levels, the presence of nutrients in water and micro-organisms that are able to form biofilm in bulk water collectively enables a conducive environment to develop biofilm on the wall surface of the pipes in the water treatment and distribution systems (Abe, 2012). Consumer demand of final water determines how long the water could be stagnant within the plumbing system, thus leads to change in microbes due to regrowth (Xu et al., 2018).

2. 5. DISTRIBUTION WATER CHALLENGES

Raw water is being treated through the drinking water treatment plants and pumped into the drinking water distribution network to provide safe water to the consumers in adequate quantity and quality (Van der Walt et al., 2021). The design of water distribution system consist of pipes, pumping system, fittings, facilities for water storages and installed devices that are used to avoid back-flow (Zhang et al., 2017).

Water quality in post-treatment depends mostly on the characteristics of the distribution system and the conditions in which it's being operated (Li et al., 2019). The quality of the tap water is solely dependent on the pipes that flows through (Zhang et al., 2017). Depending on the flows and other factors, biological substances establish their community in the distribution network and this lead to the formation of biofilms and microbiological regrowth (Tiruneh et al., 2019). Also, to a certain extent, microorganisms establish their community in the biofilms because they derive or acquire nutrients from the biofilms and moving water (Monteiro et al., 2014.). Microorganism that are attached to the biofilm of the municipal water distribution pipes are a provocative factor in supplying safe water (Nono et al., 2018). Specifically, the biofilms in water distribution network promotes a conducive living environment for bacteria, archaea, fungus and protozoa (Kelly et al., 2014). The presence of bacteria on the biofilm in distribution system produces soluble microbial products (SMP), such proteins which accelerate disinfectant decay and concomitantly contributes to the formation of disinfectant by-products (Li et al., 2019).

Pipe corrosion and taste odor in the distribution system is mostly influenced by the presence of biofilm in the distribution network (Nono et al., 2018). Bacteria self-attach on the surface of the suspended particles in such a way that the disinfectant could not reach (Saidan et al., 2017). When hydraulic properties such as (flow velocity or back flush and more) of the system is disturbed, the suspended particles are being released to the bulk water (Kowalska et al., 2006, Rubulis et al., 2008).There is insufficient knowledge regarding the composition of species and ecology of biofilms within distribution system, since well it is challenging and costly to get samples from underground pipes (Parsek and Singh, 2003).

A low number of suspended particles can still exist in the water distribution system due to being partially removed from the raw water treatment and the contaminants that are found in reservoirs or pipes (Dang and Jayaretne, 2014, Kelly et al., 2014).The final water mainly carries along little concentrations of organic carbon, inorganic nutrients, and chlorine residuals (Kelly et al., 2014).

Disinfection by-products are formed when chlorine is reacting with inorganic and organic matters during the transportation of water within the distribution system (Nono et al., 2018). The contributing factors towards disinfection byproducts are mostly the water pH, temperature, contact time, type, and concentration of chlorine (Chowdhury, 2009).

The bulk and wall chlorine decay in water distribution systems are very complex and vary from one distribution system network to the other (Monteiro et al., 2017). These factors are being characterized by the age of the system, type of pipes, biomass on the wall surface, hydrodynamics and fluid flow of the network (Chen et al., 2020). It is critical to understand the factors that contributes to the chlorine decay in the

affected distribution network and best model the bulk chlorine decay before the wall decay studies (Angelouds A, 2014).

2. 6. TYPES OF DISINFECTANTS AND OXIDANTS.

There are several water disinfectants or chemicals that are dosed in the water to destroy pathogens that are harmful for consumers. Chemical oxidants are disinfecting techniques that are used to oxidize natural organic and inorganic matters in water.

2. 6.1 Chlorine gas

A greenish-yellow chlorine gas is widely used in the process of disinfecting water for both primary and secondary disinfection. By employing chlorine to water ensures the effectiveness role of nearly killing all the pathogenic microorganisms found in the water (Krishna and Sathasivan, 2020). The production of chlorine gas involves passing of a brine solution has through electrolysis in a diaphragm, membrane or mercury cell as shown below:

$$2NaCl_{(aq)} + 2H_2O_{(g)} \rightarrow 2NaOH_{(aq)} + Cl_{2(g)} + H_{2(g)} \quad \text{(Eq.2.1)}$$

The brine in Eq. 2.1 decomposes to sodium hydroxide, chlorine gas and hydrogen gas. The process of chlorination is not costly as compared to Ultraviolet or Ozone disinfection methods and the chlorine dosages can be easily controlled (Khayyat, 2000). Chlorine gas is harmful when is being inhaled at a concentration of between 3-5 mg/L and it is fatal when a human being is exposed to a 4 mg/L for an hour. Chlorine gas in water treatment can be applied during the pre-chlorination, re-chlorination, post-chlorination and de-chlorination stages (Kowalska et al., 2018). The application of chlorine in water is to control microorganisms, remove ammonia (NH_3), controlling the water taste and odor, the reduction of watercolor, destroying

organic matters and the oxidation of: hydrogen sulfide (H_2S), iron (Fe^{2+}) and Manganese (Mn^{2+}). Chlorine gas is highly reactive and effective in water disinfection, however the reactivity is pH dependent (Ishaq et al., 2018).

2. 6.2. Chlorine dioxide

Chlorine dioxide (ClO_2) is a water disinfectant that is being used worldwide to inhibit the regrowth of micro-organisms and bacteria in municipal water. It is also used as a pre-oxidant to extract water taste, odor, colour, phenol, iron (Fe^{2+}) and Manganese (Mn^{2+}) during the pre-disinfectant stages of water treatment (Gomes et al., 2016). production of chlorine dioxide involves the reaction of sodium chlorite with acid as shown in Eq.2.2:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \quad \text{(Eq. 2.2)}$$

Chlorine dioxide gas is highly volatile and hence it can be only produced onsite in small quantities using special reactors. For safety and health purposes, chlorine dioxide gas dosages in large quantities are prohibited and can be used at the point of use. The instability of chlorine dioxide is much better as compared to ozone and the residual does not last long (Hua et al., 2015a).

There are less chlorinated compounds generated after reacting with natural organic matters and its effectiveness is independent of water pH. Chlorine dioxide is efficient in eliminating the contaminants that are harmful to consumers and requires four (4) hours of reaction time in low dosage (Hallam NB, 2002). It is 99% more efficacious in destroying viruses as compared to bacteria. Chlorine dioxide is a strong oxidizing agent, does not react with the ammonia available in the water and have no effect in producing Trihalomethanes (Ishaq et al., 2018).

2.6.3. Sodium hypochlorite solution

Sodium hypochlorite (NaOCl) is mostly employed as a bleaching agent for paper or textiles bleaching and as a water disinfection. Chlorine concentration in the solution varies between 10-15% as free chlorine and the addition of hypochlorite in water produces the hypochlorous acid as shown below (Gomes et al., 2016):

$$NaOCl + H_2O \rightarrow HOCl + NaOH^- \quad \text{(Eq. 2.3)}$$

The hypochlorous formed in Eq.2.3 is defined as a free available chlorine (FAC) and is further separated to hydrochloric acid (HCl) and Oxygen (O) as an effective oxidizing agent. The efficacy and reactivity of sodium hypochlorite is similar as compared to chlorine gas, however chlorine in the hypochlorous acid quickly loses its effectiveness during the process of solution storing (Rodrigues et al., 2013).

2.6.4. Calcium hypochlorite

Calcium hypochlorite ($Ca(ClO)_2$) is a water disinfectant that have the similar effects as sodium hypochlorite and calcium hypochlorite mostly available in solid with 70% of chlorine than liquid sodium hypochlorite (Debordea and Guntena, 2008). The formation of chlorine from calcium hypochlorite is shown as the following Eq.2.4

$$Ca(ClO)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2 \quad \text{(Eq. 2.4)}$$

Compared to chlorine gas and sodium hypochlorite, calcium hypochlorite is user friendly and has an exceptional stability to protect its strength gradually when stored in a dry place (Ishaq et al., 2018). The hypochlorous acid produced in Eq.2.4 have the same chlorine reactivity as of sodium hypochlorite with 99% of destroying all contaminants in the water (Cong et al., 2017).

2. 6.5. Chloramines

The excess of free available chlorine (FAC) with the reaction of ammonia generates the formation of chloramines at a theoretical pH of 8.4 as shown in Eq.2.5 (Liu et al., 2014),

$$NH_{3(aq)} + HOCl \rightarrow NH_2Cl + H_2O \quad \text{(Eq. 2.5)}$$

Chloramines performs a crucial role in the distribution system by ensuring that residual protection is maintained. Compared to chlorine, chloramines have a higher stability and produce less of halogenated by-products (Ishaq et al., 2018). The chloramines reacts with other micro-organisms and inhibit the survival of bacteria, however the reaction rate is very slow as compared to chlorine (Krishna and Sathasivan, 2020).

2.6.6. Ozonation

Ozone is a water disinfectant that has been used widely in wastewater and water reuse applications. Liquid oxygen is passed through ultraviolet light to produce ozone molecule as shown below (Morrison et al., 2022):

$$3O_2 \xrightarrow{hv} 2O_3 \quad \text{(Eq. 2.6)}$$

The formed ozone gas is a highly reactive oxidant, destroys organic matters; viruses, bacteria and eliminates water odor or taste. Ozone is a better water disinfectant as compared to chlorine, there is no formation of disinfectant by-products and residuals. The ozonation process produces a multitude of carbonyl disinfection byproducts. However it is a very expensive technique and requires a sophisticated operating equipment (Morrison et al., 2022).

2. 6.7. Ultraviolet light (UV)

Ultraviolet light is widely used to disinfect wastewater, drinking water and aquaculture. The UV light kills the biological microorganism components by breaking the chemical bonds in DNA,RNA and proteins (Ishaq et al., 2018).

2.6.8. Photocatalysis

Photocatalytic disinfection in water disinfection is being used widely for having exceptional benefits of using sunlight during the process and a solid catalyst like (TiO_2) titanium dioxide is used (Dalrymple et al., 2010).

2. 7. ROLE OF CHLORINE IN WATER TREATMENT

The significance of using chlorine in water treatment plants will be broadly highlighted in this section.

2. 7.1 Aqueous chlorine chemistry

Gaseous chlorine Cl_2 or hypochlorite are mostly used during chlorination processes in water treatment, the following equation describes the hydrolysis of chlorine in water (Debordea and Guntena, 2008):

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad \text{(Eq. 2.7)}$$

The hypochlorous (HOCl) acid produced from reaction Eq.2.7 is a weak acid that rapidly dissociates in aqueous solution (Debordea and Guntena, 2008):

$$HOCl \rightarrow H^+ + OCl^- \quad \text{(Eq. 2.8)}$$

2. 7.2. Organic compounds

Organic nitrogen compounds are found in wastewater that are being originated from domestic use (Pretorius and Pretorius, 2001). Chlorine reacts with olefins,

oxygenated moieties (alcohols, aldehydes ,ketones and acids), sulfur containing moieties, nitrogen containing moieties and aromatic compounds (Debordea and Guntena, 2008). The reaction of chlorine and organic nitrogen produces N-chloro compounds or chloramines that have a high stability and in that case, the chloramines can bot be effectively oxidized during the chlorination process and formation of disinfection by-product occurs (Pretorius and Pretorius, 2001).

2. 7.3. Inorganic Compounds

The most valuable properties of free chlorine is that of being a very strong chemical oxidant and the reactiveness of free chlorine solely rely on the water pH (Pretorius and Pretorius, 2001). In the process of aqueous chlorination, hypochlorous acid reacts with Ammonia, Halides, other anionic inorganic compounds (SO_3^{2-}, CN^-, NO_2^- or sulfide), As (II), Iron Fe (II), and Mn (II). The hypochlorous acid oxidizes all the inorganic compounds to their respective oxidized compounds, such as Fe(II) being oxidized to Fe(III) (Debordea and Guntena, 2008).

The inorganic compounds found in wastewater treatment are complex chemicals and rapidly consume 90% of free chlorine. The overall chlorine reactive compounds is being represented by the following reaction (Pretorius and Pretorius, 2001):

$$Cl_2 + H_2O + (\text{Chlorine demand}) \rightarrow 2HCl + (\text{Oxidized compounds}) \quad \text{(Eq. 2.9)}$$

However, hydrochloric acid generated from equation 2.9. continue to react with the alkalinity of the water as indicated in the following equation (Pretorius and Pretorius, 2001):

$$2HCl + H_2O + CaCO_3 \rightarrow CaCl_2 + CO_2 + 2H_2O \quad \text{(Eq. 2.10)}$$

The above reaction indicate that chlorination of water can result in a pH shift provided that the alkalinity of the solution is insufficient to buffer the reaction (Pretorius and Pretorius, 2001).

2. 8 EFFECTS OF CHLORINE AS A POST DISINFECTANTS

The commonly used disinfectant worldwide is chlorine for being cost effective and having the capacity to prolong residual chlorine within the water distribution system (Alexandrou et al., 2018). Chlorine reacts with bromide ion and dissolved organic matter in the system hence possible health threatening disinfection products like, trihalomethanes (THMS) and halo acetic acids (HAAS) could be produced (Abokifa et al., 2019).

Controlling desired chlorine residual in the system requires booster doses (re-chlorination) to generate a higher dosage at the inlet and this will be reduced at the exit point, however, a high dose of chlorine produces taste or odor at the upstream and complaints from consumers arise (Hua et al., 2015a). The chlorine dose should be sufficient enough to inactivate pathogens and the residual should be minimum to limit generation of disinfectant by-products and prevent bacterial growth (Goodarzi et al., 2020, Hua et al., 2015a).

It is required by water quality regulations to maintain sufficient chlorine residual within the distribution. However, water treatment processes, water quality and the state of the distribution system are the driving force towards the chlorine decay (Kophaei and Sathasiva, 2011).

2. 9 REGULATORY REQUIREMENTS

The formation of disinfection by-products varies worldwide, various disinfection by-products (DBP) have been regulated by the water health organization (WHO) and

the most prominent DBP species are the Trihalomethanes (THMs), Halo acetic acids (HAAs) and Halo acetonitrile (HANs) groups. According to WHO, the required concentrations of THMs, HAAs and HANs are 0.3,0.02 and 0.002 mg/L respectively (Alexandrou et al., 2018). In South Africa, the allowed concentrations of organic compounds such as THMs are 0.2 mg/L and 10 mg/L for total organic carbon, for Inorganic compounds like iron and sulphate was found to be 0.2 and 0.4 mg/L respectively to mention few (Mamba et al., 2008). Maintaining chlorine residual in the distribution is necessary to prevent water contamination and the recommended concentration of chlorine residual by WHO is between 0.2-1.0 while in South Africa it is found to be 0.005 mg/L (Mamba et al., 2008, WHO., 2011).Table 2.1 summarizes the maximum allowed concentrations of Inorganic compounds that are regulated by the South African water governing bodies

TABLE 2.1. Regulatory limits for portable water inorganic chemical parameters in South Africa(Mamba et al., 2008).

Determinant	**Value (mg/L)**	**Determinant**	**Value (mg/L)**
Aluminum (Al)	0.3	Lead	0.02
Ammonia	1.0	Manganese	0.1
Antinomy	0.01	Mercury	0.001
Arsenic	0.01	Nickel	0.15
Chromium	0.1	Sodium	0.2
Copper	1.0	Zinc	5.0
Iron	0.2	Chloride	200
Cyanide	0.05	Fluoride	1.0
Sulphate	400	Selenium	0.02
Nitrate	10	Nitrite	10

2. 10 CHLORINE DECAY

2.10.1. Chlorine decay in water distribution network

Chlorine decay is the process in which chlorine is being consumed by reacting with chlorine reactive substances that includes bacteria regrowth, cells inactivation, and chemicals leading to the formation of variety of disinfection by-products in drinking water distribution system (Clark, 2015, Wang et al., 2019). Furthermore, chlorine decay is accelerated by the reaction of chlorine with pipe deposits that are formed during biomass growth and corrosion. Prediction of chlorine decay or chlorine decay modelling in large water distribution systems is challenging since it depends on the hydraulic conditions of the system (Kowalska et al., 2006).

The chlorine decay model consists of two reaction mechanisms: the reaction of chlorine with bulk water and pipe wall (Hua et al., 2015a). Chlorine decay model considers the reaction rate of chlorine with bulk water (k_b) and the reaction rate of chlorine with the pipe walls (k_w) (Garcia-Avila et al., 2020).

2.10.1.1. Bulk decay reaction mechanism

The reaction rate of bulk decay should be distinguished from wall decay by analyzing chlorine decay experiments of the water source at controlled conditions such as temperature and reactant concentrations in a laboratory (Cong et al., 2017). Bulk decay rate is being determined by timeously tracing the chlorine concentration using glass bottles that are already filled with the sample water. Inverse relationship between the bulk decay coefficient and initial chlorine concentration was discovered in the laboratory analysis (Kowalska et al., 2018, Powel et al., 2000).

This illustrates that if chlorine dose is being increased in a system, therefore the bulk reaction rate decreases leaving more chlorine residual in the water. However the

more chlorine residual that exceeds 0.5 mg/L it is highly chronic for consumption as declared by the world health organization (WHO., 2011). In controlling the chlorine residuals within the distribution systems, bulk chlorine decay models and simulations are continuing to be developed and optimized to control bulk chlorine decay (Cong et al., 2012).

2.10.1.2. Wall reaction mechanism

It is necessary to recognize the interaction between biofilm (biomass) formation and the chlorine demand for the reaction prior to model chlorine decay (Kowalska et al., 2018). After determining the bulk decay rate from laboratory tests, the wall decay rate is established through a calibration process that determines the difference of chlorine consumed within the distribution system and the chlorine consumed through bulk decay tests (Fisher et al., 2017).

However, the chlorine decay coefficient at the wall solely rely on the conditions of the pipe flowing in and also the pipe materials (Tiruneh et al., 2019). The ratio of surface to volume ratio (S/V) also contributes to the chlorine decay within the pipe walls. When increasing the ratio of S/V so does the inner pipe surface in contact with chlorine residuals increases (Wen et al., 1999).

2.10.2. Chlorine decay models

Insufficient knowledge on the kinetics of chlorine reaction in water distribution is a challenge and the following reaction describes the foundation of chlorine decay models (Cong et al., 2012):

$$\mathrm{Cl} + \mathrm{reactants} \rightarrow \mathrm{products} \qquad \text{(Eq. 2.11)}$$

In the above reaction, Cl represents chemical chlorine residual and reactants describes the chlorine demand species to form disinfection by-products as represented by products (Cong et al., 2012).

2.10.2.1 Zero Order model

Zero order reaction kinetic model takes place when the reaction rate in the system remains constant and the limiting reactant is not chlorine. Zero-order model is used mostly in chlorine decay models that involves corrosion of cast iron pipes (Monteiro et al., 2020). The following equation describes the zero-order reaction kinetics of chlorine in water:

$$Cl(t) = Cl_0 - k.t \quad \text{(Eq.2.12)}$$

Here, chlorine concentration at time t(h) is being represented by Cl(t) in (mg/L) while Cl_0 represents the initial chlorine dose (mg/L) and k is the decay rate (mg/L.h) (Ralph et al., 2007).

2.10.2.2 First Order model

The first order reaction kinetic model takes place when the chlorine concentration is the limiting reactant when reacting with chlorine reactive substances in both wall and bulk decay rate. For first order model, the chlorine decay rate rely mostly on the initial chlorine dose concentration and not depending on the detected chlorine demand (Fisher et al., 2017, Garcia-Avila et al., 2020).

Chlorine concentration relies on the mass transfer rate from bulk flow to the pipe walls and it is in equivalent proportion with the chlorine residual. Film resistance model represent the mass transfer process when chlorine is being transported from the bulk flow to the pipe walls at a proportional rate to the slope of chlorine decay rate (Boccelli et al., 2003, Monteiro et al., 2020). The first order reaction rate model and the overall decay rate is being presented by the following equations Eq.2.13-14:

$$Cl(t) = Cl_0 e^{-kt} \quad \text{(Eq.2.13)}$$

$$K = k_w + k_b \quad \text{(Eq. 2.14)}$$

Where chlorine concentration at any given time is being represented by Cl(t) (mg/L), Cl_0 represents the initial chlorine dose(mg/L) and K represent the first order over all decay rate coefficient of chlorine (mg/L.h), while k_w and k_b represents the wall and bulk decay rate coefficients respectively (mg/L.h) (Cong et al., 2012).

2.10.2.3 Second Order model

The second order model kinetics includes a two components irreversible reaction during chlorine reaction with organic matter. The two components second order model constitutes for both chlorine and chlorine reactive substance through the irreversible reaction, the following reaction describes the second order chlorine decay model (Boccelli et al., 2003):

$$\mathrm{Cl(t)} = \frac{\mathrm{C_0(1-R)}}{\mathrm{1-R.e^{-u.t}}} \qquad \text{(Eq. 2.15)}$$

Here the chlorine concentration at time (t) is being represented by Cl(t) (mg/L), C_0 is the initial chlorine concentration and t represents the reaction time(min). R represent the model parameter that is dimensionless and needs to be estimated , and u represent the reaction rate(1/min) (Monteiro et al., 2014., Robert and Clark, 1996).

2.10.2.4. The n^{th} order model.

$$Cl(t) = \left(k.t(n-1) + \left(\frac{1}{C_0}\right)^{(n-1)}\right)^{\frac{-1}{n-1}} \qquad \text{(Eq. 2.16)}$$

The Cl(t) represent the chlorine concentrations(mg/L) at time t(min), while n is the reaction order model, C_0 is the initial chlorine dose(mg/L) and k is the bulk decay coefficient(1/min)

2.10.2. 5. Determining the bulk reaction order of the samples

The measurements of chlorine residual lab test and their respective time intervals should be plotted graphically to determine the relationship. A zero-reaction order

relationship is when the measured residual chlorine and time plot gives a straight line. A first reaction order relationship is when the measure chlorine residual takes a natural log or ln(C) against time gives a straight line. A second reaction order relationship is when the measured chlorine as (1/C) plotted against time and thus gives a straight line (Garcia-Avila et al., 2020).

2.10.3. The limitations of traditional chlorine decay models

Modelling first order chlorine decay is easy and possible due to only defining a singular parameter (bulk decay rate (k)) through analytical experiments and assuming that chlorine reacts with a singular substance (Cong et al., 2017). First order chlorine decay models are dependent on the chlorine concentration as a limiting factor, hence this models has not produced accurate results because chlorine reacts with multitudes of chlorine reactive substances (Tiruneh et al., 2019). The n^{th} order and parallel order chlorine decay models were proposed to improve the accuracy of first order models by accommodating the reaction in both slow and fast decay phases (Cong et al., 2017), however, this models did not produce accurate results that were fitting with the analytical experiments and not accumulating the effect of the rapid chlorine dose well, even though parallel first order model was the best, it did not yield enough results to fit the analytical data (Powel et al., 2000). This models are less effective and does not produce accurate results for drinking water due to the assumption that the concentration of available chlorine is not sufficient enough to react with the chlorine reactive substances completely (Phillip M, 2009, Rossman et al., 1994, Saidan et al., 2017).

The second order chlorine decay models are based on the effect of chlorine reacting with another unknown chlorine constituent. The limitation of second order chlorine decay model is that the concentration of free chlorine should not be the same as the

concentration of the singular chlorine reactive substance. In most cases, chlorine reacts with more than one chlorine reactive substance hence this model is also not sufficient to define the chlorine decay in both slow and fast decay phases. However, second order chlorine decay models are better when compared to first order chlorine decay models (Jamwal and Kumar, 2016, Kastl. G.J., 1999, Kowalska et al., 2018).

2.11 EXPERIMENTAL APPROACH

2.11.1 Bulk Chlorine decay using analytical methods.

2.11.1.1. The effect of water indexes (Dissolved Organic Carbon, UV_{254}, Ammonia and EEM)

Water quality indexes play a significant role in chlorine decay modeling, Wang et al. (2019) analyzed the effect of dissolve organic carbon (DOC), UV_{254} , ammonia and ultraviolet absorption (UV_{254},), pre-ozonation using ferric sulphate and aluminum sulphate as coagulants and synthesized water to investigate the effect of pre oxidation especially in the essence of removing dissolved organic carbon (Wang et al., 2019).

In the study of Wang et al. (2019), the chlorine decay established from the chlorine consumption in a period of 8 hours found that the treatment system that included lower pre-ozonation and coagulant concentration of ferric sulphate resulted in the best chlorine stability and THMs below 0.06 mg/L followed by the ferric sulphate coagulant, however the (DOC), UV_{254}, EEM and ammonia did not constitute to chlorine decay. The study of Wang et al. (2019) strongly suggested that pre-ozonation assist in stabilizing chlorine residual.

Bu et al. (2019) has investigated the effect of using coagulation and pre-ozonation to remove the natural organic matter (NOM) and determine the formation of

disinfection by-products. In their study, it was found that the addition of ozone after the coagulation dosage has increased the removal of NOM by achieving a less UV_{254} that was below 0.023 cm^{-1} and the dissolved organic carbon (DOC) were below 2.31 mg/L while the coagulant dose was set to 7 mg/L. However, the formation of disinfection by-products were established after the addition of sodium hypochlorite (NaOCl). The coagulation after ozone has performed better results, since well the coagulant after ozone stabilizes the formation of DBPs especially for water that contains Bromine and the chlorine dosage had no impact on forming DBPs (Bu et al., 2019). It is critical to perform pre-ozonation as a pre-treatment technique that will stabilize the chlorine residual after chlorination (Fan et al., 2019).

2.11.1.2. The effect of natural organic matters towards chlorine decay

Krishna et al. (2020) studied the effect of chlorine tablet-dosed towards the bacterial community that includes opportunistic pathogens and nitrifies. In their study, the selected bacterial groups were Methyl bacterium, Hyphomicrobium and unclassified Rhizobia. Samples were collected from the entry and exit point of the downstream of a reservoir where chlorine tablets were dosed timeously. It was found in their studies that the bacterial group dominated 93.8 % of bacterial genera in the downstream of the distribution pipelines and E. coli was not detected in the period of the study (Krishna et al., 2020).

The dosages of chlorine tablets had a very positive impact towards increment of total chlorine to the ratio of total ammoniacal nitrogen (TAN), notwithstanding the slightest changes of total chlorine residual. The total chlorine residuals and status of nitrification did not have an impact on the excess of bacterial community (Krishna et al., 2020).

2.11.1.3 The effect of temperature and pH

Powel et al. (2000) studied the factors that contributes to chlorine decay within distribution systems. It was revealed that the bulk decay coefficient of chlorine decay has shown a dependence on temperature, initial chlorine dose and total organic matters. There was no effect of pH towards bulk chlorine decay coefficient observed since the pH variance were minimum (Powel et al., 2000).

Zhang and Andrews (2012) has investigated the effect of pH using samples that had three pH values (6.6, 7.6 and 8.6), and there were no statistical variation in their findings and the pseudo-first order bulk decay chlorine coefficients were found to be ranging between 0.0018 to 0.0022 (1/hour) (Zhang and Andrews, 2012).

2.11.2 Wall chlorine decay using analytical methods.

2.11.2.1 The effect of biofilm

Biofilm formation on the pipe walls accelerates the chlorine decay in the water distribution system. Xu et al. (2018) investigated the effect of biofilms growth towards chlorine decay and TTHM formation that prevails during physical and chemical water treatment processes. Pipe loop system of poly vinyl chloride pipes were used to resemble the distribution system and the system was checked after every two weeks. The biofilm development in the pipe loops allowed enough time to occur, then the pipes were removed from the system and organic-free chlorine solution buffer was added to the pipes for a period of 48 hrs. It was found that the chlorine decay in the pilot study was higher than the real distribution systems. Biofilms have a great impact in chlorine decay within distribution system by generating toxic disinfection byproducts (Xu et al., 2018).

Chen et al. (2020) investigated the chemical and biological threat during the expansion of water distribution pipe renewal. The sole concerned parameters were

the disinfection by-products (DBPs) and the potential for disinfection by-products (DBPsFP) over a period of two years. It was found that the total bacterial count in the new pipelines ranged from 1.38 to 9.9 x 10^8 per cm^2. The potential for disinfection by-products slightly varied at both front and back ends. Stainless steel pipes were found to have less biofilm growth as compared to ductile and galvanized pipes. The total DBPsFP of biofilms were found to be the highest as compared to the DBPs (Chen et al., 2020).

2.12 SIMULATIONS AND MATHEMATICAL ESTIMATES

2.12.1 Bulk chlorine decay rate using simulations and mathematical estimates.

2.12.1.1 The effect of temperature on bulk chlorine decay rate (NOM and THMs)

Monteiro et al. (2015b) has investigated the effect of temperature changes towards chlorine decay rates for raw and final water from various locations. The model was based on the variation of natural organic matters concentration (NOM) and to establish the effect of temperature towards fast and slow decay rates using two reactant models (2R). It was found that in both raw and final water, the bulk chlorine decay coefficients in fast and slow decay phases were extremely impacted by the temperature variations. The slope of Arrhenius equation for the slow decay phase were found to be the highest and highly sensitive towards temperature as compared to the fast chlorine decay phase (Monteiro et al., 2015b).

Furthermore, Abokifa et al. (2019) studied the effect of temperature towards the formation of THMs using a multiple species reactive transport model. The temperature varied from 0 °C to 30 °C, it was found that temperature has an influence on the formation of bacterial regrowth while temperature increment affected various parallel processes. Temperature increment from 0 °C to 25 °C

activates; the exponential growth of bacterial community, faster consumption of chlorine residuals and the rapid depletion of chlorine reaction with biomass that generates higher concentrations of THMs (Abokifa et al., 2019).

2.12.1.2 Influence of hydraulic conditions

Jamwal and Kumar (2016) investigated the effect of flow velocity and initial chlorine levels to predict the chlorine decay coefficients using a first order model. The initial chlorine dose (IC) was at 3 and 6 mg/L while the velocity was ranging from 0.03 to 0.12 m/s. Their study has shown that the average bulk chlorine decay coefficient at IC of 3 mg/L was double as compared to the bulk decay coefficient for initial chlorine dose of 6 mg/L. This implies that the chlorine consumption in the low velocity phase was due to the effect of fast and slow chlorine reactive substances that were present in the pipe (Jamwal and Kumar, 2016).

Additionally, Abokifa et al. (2016) investigated the effect of flow velocity towards the formation of biofilm using a multiple species reactive transport model. It was found that when the flow velocity increases the enhancement of mass transfer of solutes from the bulk water to the biofilm interface was established. At elevated shear stress rate, the biomass gets detached from the biofilm or pipe wall to the bulk water. A Blasius equation was established to predict the shear stress under turbulent flow conditions and it was found that the shear stress increases with flow velocity to a power above 1 (n>1) (Abokifa et al., 2016).

Van der Walt et al. (2021) investigated the effect of water age in Sedibeng water distribution system using EPANET software. The model order of the reaction kinetics was first order, it was found that the maximum water age within the system to be 160 hours in a 70 kilometers long pipe network. The summer chlorine decay rate was found to be 0.052 (1/h) and 0.027 (1/h) during winter seasons. The simulated

chlorine model was used to optimize the disinfection systems and a switch to using ClO_2 as a disinfectant was demonstrated in order to stop the re-chlorination processes. However the use of ClO_2 as their disinfectant will require a capital of extra 100,000 Us dollars (Van der Walt et al., 2021).

2.12.1.3 The initial chlorine dose effect on bulk decay rate.

In controlling the chlorine residuals within the distribution systems, bulk chlorine decay models and simulations are continuously being developed and optimized to control bulk chlorine decay according to the review of Li et al. (2019). Furthermore, Tiruneh et al. (2019) has studied the chlorine reactive substances based on chlorine demand and total chlorine using mathematical estimates, in their studies it was found that instantaneous chlorine decay happen within 5 minutes and the bulk reaction rate relationship with initial chlorine dose was found to be inverse using mathematical estimates that was validated by the analytical results (Tiruneh et al., 2019).

2.12.2. The Rate Constant of Chlorine Decay with the Wall of Water Pipe.

2.12.2.1. The effect of hydraulic conditions

Cong et al. (2012) determined the reaction rate constant of chlorine decay at the wall by running pilot study experiments using various flow velocities that were ranging between 0.1 to 0.5 m/s, the temperatures were varying from (15, 20 and 30 °C), the initial chlorine dose concentration was ranging from 0.30 to 0.40 mg/L and the Total organic carbon (TOC) concentration was ranging from 3.5 to 5.5 mg/L. It was found that the chlorine decay coefficients of both bulk water were almost the same as the constant of the overall decay, implying that wall decay could be

approximated to zero illustrating that there was no mass transfer with the pipe wall since well the molecular diffusivity of the model were laminar flow (Cong et al., 2012). Additionally, Jamwal and Kumar (2016) determined the effect of flow velocity and initial chlorine levels to predict the chlorine decay coefficients at the wall using a first order model. The flow velocity within the pipe loop ranged from 0.02 m/s for laminar flow to 0.12 m/s for turbulent flow. It was found that the wall decay coefficient was influenced by both initial chlorine dose and flow velocity. The transition of flow regime from laminar to turbulent resulted in an increase of wall decay coefficient by 66% due to the influence of biofilm(Jamwal and Kumar, 2016).

Goodarzi et al. (2020) has investigated the effect of temperature towards flow within a chlorine contact tank using solute transport model. Reynolds-averaged Naiver-Stokes (RANS) modelling equations coupled with turbulence closure model were used to define the flow properties in a three-dimensional (3D) advection-diffusion interface. Small temperature and inflow change have impacted the chlorine concentration within the tank. Their study demonstrated that the chlorine decay in the tank was linearly dependent on the temperature, since when the temperature increases also the chlorine depletion rate was increasing, this was because of the effect that temperature has on the reaction rate as described by the Arrhenius equation (Goodarzi et al., 2020).

2.13 TOOLS FOR SIMULATIONS AND MATHEMATICAL ESTIMATES

This section will provide the available software packages and numerical estimates to perform chlorine decays assays.

2.13.1The integrated chlorine decay mathematical models derived from traditional models

The integrated chlorine decay models are finite reactants models that are grounded based on chlorine reactive finite components that includes single reactant (SR) second-order model, two reactants (2R) second order model and variable rate coefficients model (Fisher et al., 2012).

These models produce accurate results as compared to the traditional chlorine decay models. However, the challenge arise when measuring the concentration of the finite chlorine reactive substances since it cannot be measured directly implying that the model parameters can be produced from fitting the experimental data to the models and this is complex to an extent that other model parameters are being omitted for simplicity purposes (Monteiro et al., 2017, Wang et al., 2019).Some of the integrated chlorine decay models are shown in Table 2.2.

TABLE 2.2 A list of few proposed intergarted chlorine decay models in the literature.

Model	Differential equation	Integrated equation	Adjustable parameters
nth Order	$dCl/dt = -k.C^n$	$Cl(t) = \left(k.t(n-1) + \left(\frac{1}{C_0}\right)^{(n-1)}\right)^{\frac{-1}{n-1}}$	k, n
Limited first order	$dCl/dt = -k(C - C^*)$	$Cl(t) = C^* + (C_0 - C^*)e^{-k.t}$	k, C^*
Parallel first Order	$dCl/dt = -k_1C_1$, $dCl/dt = -k_2C_2$ $C_{1,0} = C_0.x$ $C_{2,0} = C_0(1-x)$	$Cl(t) = C_0.x.e^{-k1.t} + C_0(1-x)e^{-k2.t}$	k_1, k_2, x
Two reactant first order model(Monteiro et al., 2020)	$dCl/dt = \frac{2\,k_w k_f}{R(k_w k_f)}C$	$Cl(t) = Cl_0.e^{\frac{2\,k_w k_f}{R(k_w k_f)}t}$	k_w, k_f, R

2.13.2 Software packages for chlorine decay simulations

The use of software packages to predict and optimize the water quality models in network pipes or reservoirs has gained more attention to improve the performance and efficiency of the hydraulic systems (Fisher et al., 2012). Mathematical, physics and chemistry concepts that constitutes to modeling of chlorine decay are being incorporated in the software packages to graphically visualize the water quality models within the distribution systems and water treatment systems.

2.13.2.1. The EPANET software

The Environmental Protection Agency Network (EPANET) software is a modelling tool that is being used worldwide to model and simulate the water quality models in the water distribution systems. The modelling tool was designed to comprehend the

water quality within distributions systems, and it can be used to simulate and analyze variety of water quality analysis. Researchers use EPANET software to design, optimize and develop the water infrastructure in order to optimally and cost effectively improve the hydraulic and water quality. EPANET multi species extension (EPANET-MSX) and EPANET real-time extension (EPANET-RTX) are the integrated modeling tools optimized from the traditional EPANET tool to improve the objectives of the software by accommodating even the integrated chlorine decay models (EPANET., 2022, Hua et al., 2015b, Monteiro et al., 2020).

2.13.2.2 The COMSOL Multiphysics software

COMSOL Multiphysics software is a multi-platform modeling tool that is designed to solve, analyze and simulate finite Multiphysics elements. This software enables a conventionally physics based user interfaces that are coupled with applications to solve ordinary and partial differential matrix equalities (Comsol., 2022). This software is used to simulate the effect of fluid flow dynamics, reaction mechanism and chlorine transport in water distribution systems for both traditional and integrated chlorine decay models (Goodarzi et al., 2020).

2.13.2.3. AQUASIM software

AQUASIM software is a water quality modeling software that solve the application of ordinary differential equations (ODEs) to optimize the estimation of model parameter values. The software fit experimented data with the estimated parameters by varying the estimated model parameters. This software is used widely in the simulation of chlorine decay reaction kinetics and tetrahalomethanes formation (Fisher et al., 2017, Kowalska et al., 2018).

2.13.2. Other modeling software

Other chlorine decay and water quality modelling software packages includes and not limited to: The H2Onet software is used to model and analyze water quality in water distribution systems and other modelling software (Kowalska et al., 2018).

2.14 CHALLENGES OF SIMULATIONS

Modelling chlorine decay rate constants at various temperature is quite a challenge since the model doesn't follow the Arrhenius model in many cases and the reaction kinetics requires simplification and if it is oversimplification and applied, therefore some model parameters are being omitted, this further contradicts the efficiency and validity of the model (Liu et al., 2014). Other modelling parameters requires further recalibration to compensate the effect of water flow changes (Fisher et al., 2012). The traditional first order and second order reaction rate having a singular reaction rate coefficient insufficiently interprets the bulk decay precisely. Integrated mathematical models have been developed to mitigate the inefficiency of the traditional models, however the integrated models are complex to an extent that other modeling parameters are being omitted to simplify the model and these models depend from types of water being treated, for example reclaimed water models are different from fresh water models. Simulating water quality models using EPANET has its limits since well the traditional EPANET software can only solve water quality model that follows the traditional reaction rate model. Hence the extensions of multi species and real-time application tools are being used to mitigate the limits, however these extensions require coding approaches that are not user friendly. The role of biofilm modeling is a challenge since well the water distribution pipes are embedded below the ground for years and reaching a sample for biofilm analysis on the pipe wall is a major challenge and pilot systems were developed to

investigate the growth of biofilm. However pilot studies are costly and they need more time to develop the biofilm along the pipelines and such biofilm constituents are season and flow conditions dependent, this further delay the process.

2.15 AVENUES FOR FUTURE RESEARCH

The bulk chlorine decay in laboratory experiments has been extensively studied relying mostly on the effect of organic matters. More studies that constitutes if not both but more extensive work on the effect of inorganic matters and develop models that could predict the concentration of inorganic constituents within the system. Water quality models have been researched extensively and validated by only experimental and pilot studies, however incorporating water quality models with pilot studies and solute transport models simultaneously will highlight some of the missing gaps in chlorine decay modeling. Various mathematical and computational models have been researched extensively and still remain complex, however comparison of at least five models each to filter out, improve and classify the best models according to the water type of modeling.

2.16 SUMMARY OF THE LITERATURE REVIEW.

Chlorine decay modeling plays a crucial role in enhancing water quality to meet the standards set by the World Health Organization. The modeling process involves various reaction rate models with numerous parameters specific to the water being modeled. However, due to the complexity and cost involved in chlorine decay modeling, it is important to establish simplicity and clear boundaries in the depth of the models.

Chlorine decay within the distribution system is influenced by numerous factors that vary based on the hydraulic systems in place. Extensive research has been conducted on chlorine decay, but it remains a complex field. To optimize the current

models and validate their effectiveness, it is recommended to compare at least five different water quality model approaches. This comparison research can help identify ineffective modeling techniques and improve the efficiency of existing models.

Furthermore, it is beneficial to categorize water quality models based on the classification of water types. This categorization can streamline the chlorine decay modeling process and reduce the required time.

Performing chlorine decay assays through laboratory analysis of temporal chlorine decay profiles aims to enhance the efficiency of chlorine residuals in the water distribution network system. However, conducting water samples every time the water quality changes is a time-consuming and labor-intensive task. Chlorine decay experiments typically require more than 24 hours to yield accurate results. The new approach in optimizing the water distribution network is to perform regression based chlorine decay models that will predict the sufficient chlorine dose to be simulated in a water quality and solute transport model to determine the depletion of chlorine with distance. The combination of regression chlorine-based water quality and solute transport models were not studied in comparison before, hence this study will outline the importance of using this techniques combined with the breakpoint chlorination techniques to determine the optimum chlorine dosage of the system and use literature to validate the models to ensure the accuracy and reliability of the models.

CHAPTER 3

MATERIALS AND METHODS

This section provides detailed description of the analytical procedures employed to determine chlorine residuals in the water distribution network. The chapter first describes the study area and outline the specific methods and techniques used to measure and analyze chlorine concentrations, ensuring accuracy and reliability of the data obtained. Secondly, this section illustrates the configurations of the water distribution network systems using COMSOL Multiphysics and EPANET software. Lastly, a comprehensive overview of how the used software tools were utilized to construct and simulate the water distribution network models is presented.

3.1. STUDY AREA

The residual chlorine decay constants were determined through a combination of experimental and numerical methods within the distribution network of Vaalkop Water Treatment Plant (WTP) located in the North West Province of South Africa. The primary function of the WTP is to provide water to various entities including mining houses, municipalities, and farmers in the surrounding area.

The drinking water supplied by the WTP undergoes a series of treatment processes in a 270 Mega Liters WTP facility. These processes include chemical dosing, sedimentation, floatation, filtration, and post-chlorination. After treatment, the water is stored in a distribution tank where the average chlorine concentration is maintained at 5 mg/L. This chlorinated water then travels through the main distribution line, which extends for approximately 30 km in length, supplying water to the designated areas.

Figure 3.1, depicts a map illustrating the Vaalkop catchment area and the location of the WTP. This visual representation helps provide a spatial understanding of the distribution network and its geographical context.

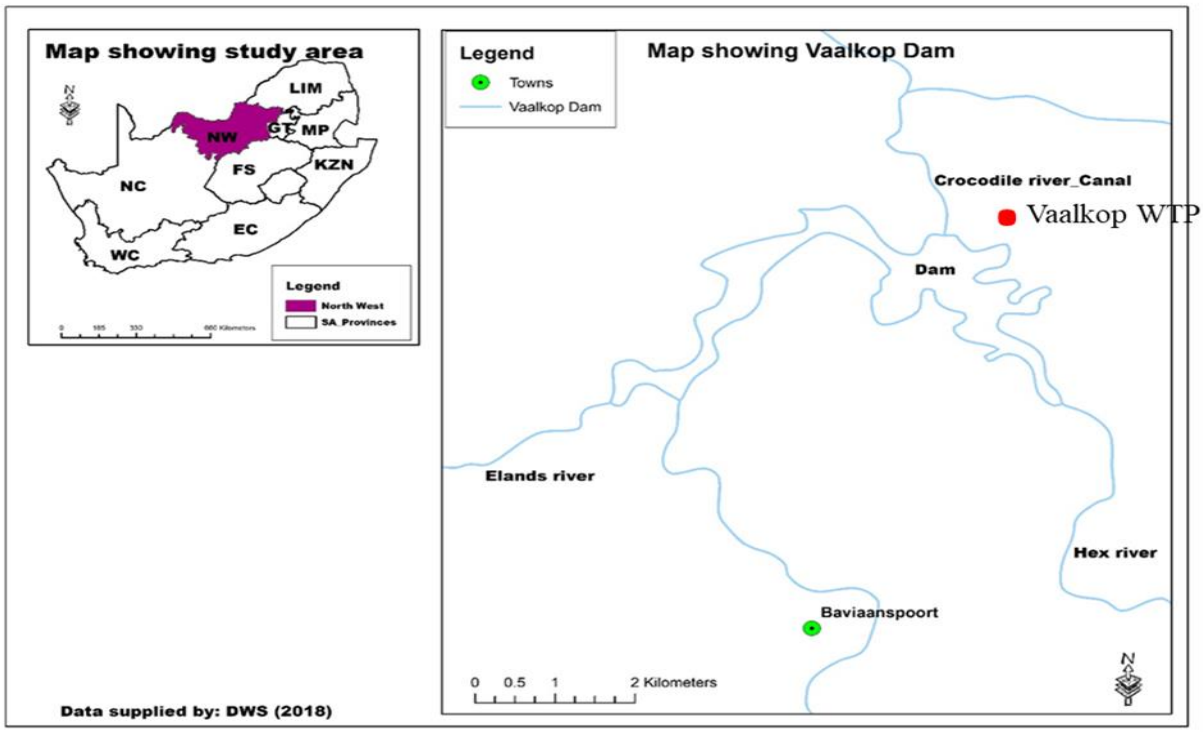

FIGURE 3.1 Location of the Vaalkop catchment and Vaalkop WTP

3. 2. ANALYTICAL ANALYSIS

3. 2.1. Collection of water (aqueous) samples

In this study, the grab sampling technique was employed to collect water samples for analysis. High-density polyethylene (HDPE) containers with a capacity of 25L were used to collect bulk water samples from the Vaalkop Water Treatment Plant (WTP). These containers are known for their suitability in preserving water quality during sample collection. For the actual water sample collection, sterilized SCHOTT DURAN® laboratory glass bottles with a volume of 1L were utilized. Before sampling, these glass bottles underwent a pre-treatment process. They were first

exposed to a 1.8% (mass per volume - m/v) solution of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), which serves as a dechlorinating agent.

3.2.2. Preparation of the working solution

In this study, high-test hypochlorite (HTH) was used as the source of chlorine. HTH typically consists of 65 to 70 percent calcium hypochlorite, with 25-30 percent available chlorine. To prepare the working solution, 70% granules of calcium hypochlorite ($CaCl_2O_2$) were used. The working solution was prepared by adding a specified amount of $CaCl_2O_2$ granules into a 1-liter container (amber container) filled with deionized water. The aim was to synthesize a solution with a concentration of 1000 ppm (parts per million) of hypochlorite. The mixture was stirred using a magnetic stirrer until the solution became homogeneous, ensuring the complete dissolution of the granules.

To achieve different desired concentrations of $CaCl_2O_2$, serial dilution was performed using the prepared working solution. This allowed for the synthesis of solutions with various concentrations of $CaCl_2O_2$ while maintaining control over the process.

To prevent unwanted reactions and ensure the stability of the chlorine, the prepared solution was stored in a dark place at a temperature of 4°C. This storage condition helps to minimize photocatalytic activities, secondary reactions, and the rapid decomposition of chlorine when exposed to sunlight.

3.2.3. Chlorine demand assays

The factor-based bench scale experiments for chlorine demand or consumption were conducted using authentic water, i.e. final water from Wallmansthal WTP. Ambient temperature, un-fortified water characteristics, and pH were considered for

this study. Ten (10) minutes of slow mixing using Phipps and Bird PB 900 Flocculation Stirrer. The PB-900 Programmable Six-Paddle Jar Tester uses four operator-programmable memory banks that offer virtually unlimited stirring capabilities. The effect of chlorine concentration was explored using six 1L containers (beakers).

The concentration was varied from 2.5, 5, 10, 15, and 20 mg/L of chlorine as High-Test Hypochlorite (HTH). The right stoichiometry for the active ingredient of the HTH were considered. Mixing was performed at 100 rpm for 10 minutes. Thereafter, aliquots were extracted for further characterization of using different equipment's. After completion of the experiments, solutions were analyzed for total and residual chlorine.

3.2.4. Chlorine decay assays

Chlorine residual was tested in 1L amber glass bottles following a procedure that was developed by Powell et al. (2000) for the bottle tests. The bottles were previously treated with 10 mg/L free chlorine in milli-Q water to remove potential chlorine demand. Each bottle was filled with 1L of water sample and chlorinated with calcium hypochlorite (HTH). Initial free chlorine concentrations were 2.5, 5, 10, 15, and 20 parts per million (ppm) or mg/L.

Thenceforth, the concentration of chlorine and water pH as a function of time was evaluated with monitoring times ranging between 0, 15, 30, 45, 60, 90, 120, 180, 1320, 1440, 4320, and 4419 minutes. Each assay, was conducted with bottles kept in the dark at controlled temperatures in an incubator. The experiment was conducted for a period of 3 days. The obtained results were then used to determine the rate at which chlorine decay in Vaalkop system as a function of time.

3.2.5. Characterization of aqueous solution

Solution pH and conductivity were measured using an HQ40d multi meter pH meter (Hach Company, Loveland, USA). The standard buffer solutions were used for calibration. Total, free chlorine and monochloramine were analyzed using MISP-REM-HAH-DR900 colorimeter (Hach Company, Loveland, USA) (Rice et al., 2012).

3.3. NUMERICAL AND SIMULATION MODELS

3. 3.1. Mathematical chlorine decay models

3. 3.1.1. First order chlorine decay model

The first order reaction kinetic model takes place when the chlorine concentration is the limiting reactant when reacting with chlorine reactive substances in both wall and bulk decay rate (Boccelli et al., 2003, Monteiro et al., 2020). The first order reaction rate model is presented in Eq. 3.1.

$$Cl(t) = Cl_0 e^{-kt} \quad \text{(Eq.3.1)}$$

Where, chlorine concentration at any given time is being represented by Cl(t) (mg/L), Cl_0 represents the initial chlorine dose (mg/L) and K represent the first order over all decay rate coefficient of chlorine (mg/L.h) (Cong et al., 2012).

3.3.1.2. Parallel first Order model

A parallel first order chlorine decay model consists of two bulk chlorine decay coefficients to account for both fast and slow chlorine decay within the water distribution pipes (Cong et al., 2012), Equation 3.2 present the parallel first order model as it is developed from the traditional first order model. The parallel first order of reaction is being expressed from:

$$C = C_0 X exp(-k_1 t) + C_0(1 - X) exp\,(-k_2 t)\,. \quad \text{(Eq.3.2)}$$

For a parallel first order model, dc/dt represents the change in chlorine concentration per unit time (mg/L.min), C_0 represents the initial dose of chlorine (mg/L), while the parameters that could be adjusted for the parallel first order model are, k_1 (1/min) which represent the decay rate coefficient of the fast reaction and k_2 (1/min) represent the slow decay rate coefficient and x is the modelling parameter (dimensionless) (Cong et al., 2012).

3.3.1.3. Second order chlorine decay model

The second order chlorine decay model kinetics consists of irreversible chlorine reactive substance through the irreversible reaction as described in Eq 3.3 (Boccelli et al., 2003).

$$Cl(t) = \frac{C_0(1-R)}{1-R.e^{-u.t}} \quad \text{(Eq.3.3)}$$

Here the chlorine concentration ate time (t) is being represented by Cl(t) (mg/L), C_0 is the initial chlorine concentration and t represents the reaction time(min). R represent the model parameter that is dimensionless and needs to be estimated , and u represent the reaction rate(1/min)(Monteiro et al., 2014., Robert and Clark, 1996).

3.3.1.4 Quantitative Chlorine Reactive substances second order model

The quantitative chlorine reactive substance model is a second order model that is developed to constitute the effect of total chlorine demand (TCD), lasting chlorine demand (LCD) and instantaneous chlorine demand (ICD) (Wang et al., 2019)as shown in Eq 3.4,

$$Cl(t) = \frac{C_{Cl,dose}-TCD}{1-\frac{LCD}{C_{Cl,dose}-ICD}.exp\left(-\left(C_{Cl,dose}-TCD\right).k.t\right)} \quad \text{(Eq.3.4)}$$

Where the Cl(t) is the chlorine residual at time t, TCD is the chlorine demand, LCD is the lasting chlorine demand, ICD is the instantaneous chlorine demand (mg/L) , k is the bulk chlorine decay rate coefficient (1/min), t is the time (min) and Cl_{dose} is the initial chlorine dosed (mg/L) (Wang et al., 2019).

3.3.1.5. The effect of regression based first order chlorine decay model.

The traditional first order chlorine decay models are being integrated with regression-based model to further the accuracy of the model by establishing an inverse chlorine, the decay rate is given by the following expression (first order).

$$\frac{1}{K} = \frac{1}{\beta} + K_0 C_0 \qquad \text{(E.q.3.5)}$$

The bulk decay rate coefficient is represented by K(1/min), the initial chlorine dose is represented by C_0 (mg/L), β (1/min) and K_0 (L.min/mg) are model parameters (Tiruneh et al., 2019).

3.3.2.5 Determining the bulk reaction order.

The measurements of chlorine residual lab test and their respective time intervals should be plotted graphically to determine the relationship. A zero-reaction order relationship is when the measured residual chlorine and time plot gives a straight line. A first reaction order relationship is when the measure chlorine residual takes a natural log or ln(C) against time gives a straight line. A second reaction order relationship is when the measured chlorine as (1/C) plotted against time and thus gives a straight line (Garcia-Avila et al., 2020).

3.3.2. Water quality and hydraulic model

3.3.2.1 Advective transport in pipes

A dissolved substance will travel down the length of a pipe with the same average velocity as the carrier fluid while at the same time reacting (either growing or decaying) at some given rate is being represented by (Rossman, 1993):

$$\frac{\partial C_i}{\partial t} = -u_i \frac{\partial C_i}{\partial x} + r(C_i) \quad \text{(Eq.3.6)}$$

where C_i represents the concentration (mass/volume) in pipe i as a function of distance x (unit length) and time t (unit time), u_i is the flow velocity (length/time) in pipe ii, and r is the rate of reaction (mass/volume/time) as a function of concentration (Rossman, 1993).

3.3.3. Dynamic chlorine decay models

3.3.3.1. Conservation of mass for chlorine

The transport of species in bulk water is described by a parallel diffusion and reaction equation from Eq 3.7-8. Since at the pipe walls, the pipe wall velocity was zero, therefore the time dependent mass balance equation of chlorine is established as (Comsol, 2022):

$$\frac{\partial C_{Cl}}{\partial t} + \nabla . J_{Cl} + u . \nabla C_{Cl} = R_{Cl}. \quad \text{(Eq.3.7)}$$

$$J_{Cl} = -D \nabla c. \quad \text{(Eq.3.8)}$$

Where C_{Cl} denotes the concentration of chorine (mol/m3), D is the diffusion coefficient (m2/s), R_{Cl} is the expression of chlorine reaction rate (mol/m3.s), u is the mass averaged velocity vector (m/s) and J_{Cl} is the chlorine diffusivity mass flux (mol/m2.s) (Bird et al., 2007, Comsol., 2022).

The chlorine decay chemical mass transport mechanism conform to the 1-D advection-dispersion reaction and while eliminating the source and sink terms, the remaining equation is being represented by Eq. 3.9 (Cunha, 2010):

$$\underbrace{\frac{\partial Ci(x,t)}{\partial t}}_{advection} + \underbrace{\frac{V_i \partial C_i(x,t)}{\partial x}}_{dispersion} + \underbrace{\frac{D\partial^2 C_i(x,t)}{\partial x^2}}_{chemical\,and\,biological\,reaction} + R[C_i(x,t)] = 0. \quad \text{(Eq.3.9)}$$

Whereby i is the pipe branch, Ci(x,t) is the concentration of chlorine at a given point in the direction (x) and time (t), Vj is the average velocity in the pipe I, D is the coefficient of the longitudinal dispersion and R(Ci(x,t)) is the rate reaction (Cunha, 2010).

3.3.3.2. The effect of fluid flow channel in bulk decay

The flow inside the pipe of water distribution system is flowing at a low velocity and is determined as laminar flow that is given by Naiver-stokes equations in Eq 3.10-Eq 3.11. (Khan et al., 2016):

$$\rho \frac{\partial u}{\partial t} + \rho(u.\nabla)u = \nabla.(-Pl + \tau) + F. \quad \text{(Eq.3.10)}$$

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho u) = 0. \quad \text{(Eq.3.11)}$$

Where ρ denotes the fluid density (kg/m3), u is the velocity (m/s) of the fluid, τ is the viscous stress tensor (Pa), F is the volume force vector (N/m3) and P is the pressure (Pa) (Khan et al., 2016).

3.4. MODEL CONFIGURATIONS

3.4.1. Water quality model configuration (EPANET)

Figure 3.2 shows a water distribution network that is equipped with a reservoir as a source, a tank at the final destination, pumps (five in total) and pipes (thirteen in total) that contributes to fourteen (14) nodes that are 5 km apart. The EPANET 2.2

model have a pipe diameter of 1 m and pipe roughness of 0.1 m. The bulk reaction order of the model were first order and second order models.

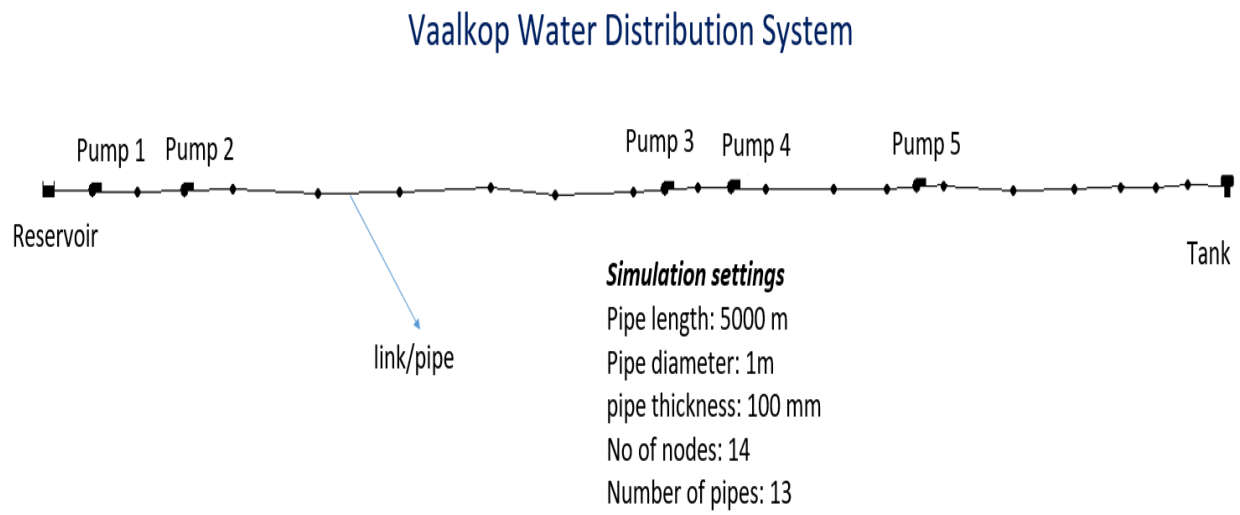

FIGURE 3.2: EPANET water quality distribution network

3.4.2. Solute transport model configuration (COMSOL Multi-physics).

Figure 3.3 shows a two dimension (2D) model geometry of a 1 m pipe long having a 0.1 m diameter. Transporting diluted species and laminar flow were used as coupled physics interfaces to simulate the chlorine decay.

FIGURE 3.3: COMSOL 2D model geometry of a 1 m pipe having a 0.1 m diameter.

A fine mesh was used and there was no slip around the boundary wall. It was assumed that the fluid was perfectly mixed at constant pressure and velocity so that the concentration throughout the system is consistent. First order and second order bulk chlorine decay models were determined and assuming that there were no reaction with wall boundaries.

3.5. QUALITY CONTROL AND QUALITY ASSURANCE

3.5.1 The quality control and assurance of experimental results.

Quality assurance and quality control was achieved through the use of internationally accepted standards in an ISO/IEC 17025:2017 accredited laboratory, i.e., at Magalies Water Services Laboratory, Brits, North West, South Africa. Experiments were performed in triplicates and the results were reported as mean values. A control experiment was established with the known theoretical concentration that has been verified analytically and this was verified from time to time to ensure that there were no changes in the concentration of chlorine in the control sample. This was done to enhance the creditability and trustworthiness of the results and operational parameters.

3.5.2. The quality and assurance of the numerical and simulated chlorine decay models.

The adopted mathematical models were guided by the experimental chlorine decay profiles determined in the laboratory and validated by the studies of other researches such as ((Goodarzi et al., 2020, Monteiro et al., 2014., Nono et al., 2018, Tiruneh et al., 2019, Wang et al., 2019) and others) . The developed water quality models and solute transport models were guided by the mathematical models and validated by the studies of other researches (Goodarzi et al., 2020). The quality of

the developed models will be controlled by experimental studies and available literature to ensure the validity and reliability of the developed chlorine decay models.

3.6. MODEL CALIBRATION.

The adopted numerical and finite element model parameters (bulk decay coefficients and model parameters) were calibrated to ensure Goodness of fit with the experimental chlorine decay profiles. Goodness of fit of the models to experimental data was assessed by coefficient of determination R^2. An error analysis is required in order to evaluate the fit of the adsorption isotherms to experimental data. In the present study, the linear coefficient of determination of R^2 was employed for the error analysis. The linear coefficient of determination is calculated by using the equation:

$$R^2 = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{n(\sum x^2) - (\sum x)^2} - \sqrt{(\sum y^2) - (\sum y)^2}} \qquad \text{(Eq. 3.12)}$$

Theoretically, the values of R^2 ranges from 0 to 1. A R^2 value of one show that 100% of the variation of experimental data is explained by regression equation. The coefficient of determination R^2 was applied to determine the relationship between the experimental data and the isotherms in most studies.

CHAPTER 4

RESULTS AND DISCUSSIONS.

This section presents the results of chlorine decay modeling, utilizing both analytical and numerical approaches. The findings obtained from the determination of chlorine decay mechanisms and the corresponding simulated chlorine decay models based on reaction orders are discussed and illustrated.

4.1. CHLORINE DEMAND, DECAY, AND pH OF VAALKOP SYSTEM

This section focuses on reporting the results of chlorine demand and decay in the Vaalkop Water Treatment Plant (WTP) system. The study utilized both experimental data and numerical modeling estimates to assess the challenges related to microbial failure at different points in the distribution system. The goal was to identify sustainable strategies to maintain adequate residual chlorine levels that can effectively suppress microbial regrowth.

The findings of this study provide insights into the chlorine demand and decay dynamics within the distribution network, shedding light on their potency in suppressing microbial regrowth and addressing distribution challenges. The experimental results, combined with the numerical modeling estimates, contribute to a comprehensive understanding of these interlocking aspects within the distribution network.

High-Test Hypochlorite (HTH) was selected as the disinfecting agent for the study. Various mathematical models, including EPANET and COMSOL Multiphysics, were employed to complement the experimental findings and further explore the intricate characteristics of the distribution network. These models serve as valuable tools for

decision-making processes, particularly in the installation of booster stations within the water distribution network. The determination of chlorine demand and decay is crucial in the water purification process, as it directly impacts the quality of water supplied to end-users. By examining these factors in the Vaalkop WTP system, this study aims to address the challenges associated with microbial failure and provide sustainable pathways for maintaining acceptable residual chlorine levels.

4.1.1. Final water chlorine demand

The schematic deduction of chlorine demand, breakpoint chlorination, and mono-(di)-chloramination feasibility for the final water produced at Vaalkop WTP are shown in Figure 4.1 below.

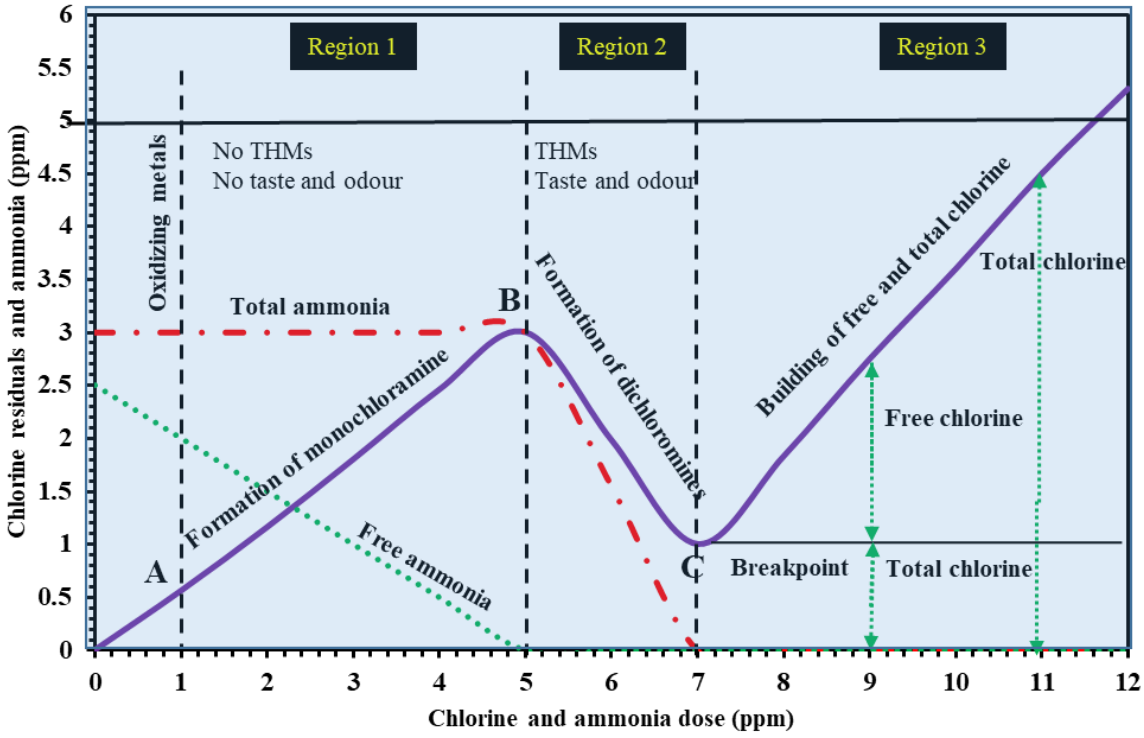

FIGURE 4.1: Schematic overview showing the chlorine demand, breakpoint chlorination, and mono-(di)-chloramination feasibility for the final water produced at Vaalkop WTP.

In water systems with a high concentration of ammonia, the chlorine gas undergoes

a reaction with the dissolved ammonia, resulting in the formation of monochloramines and various by-products. Specifically, chlorine reacts with ammonia present in the water, primarily at a chlorine to ammonia ratio of 5:1, leading to the formation of monochloramine. Subsequently, chlorine continues to react and form dichloramine, which eventually decomposes into nitrogen gas. This process follows the well-known principle of equilibrium, known as Le Chatelier's principle of equilibrium (Yang et al., 2019, Lu et al., 1993).

The presence of residual chlorine in the water system after meeting the chlorine demand ensures effective disinfection and oxidation of the water. This residual chlorine plays a crucial role in removing contaminants such as manganese (Mn), iron (Fe), and other impurities through oxidation processes. The impact of varying chlorine dosages on both chlorine residual and chlorine demand for the final water at Vaalkop WTP is studied under specific conditions, including different concentrations, 10 minutes of mixing, a mixing speed of 100 rpm, and ambient temperature and pH as shown in Figure4.2.

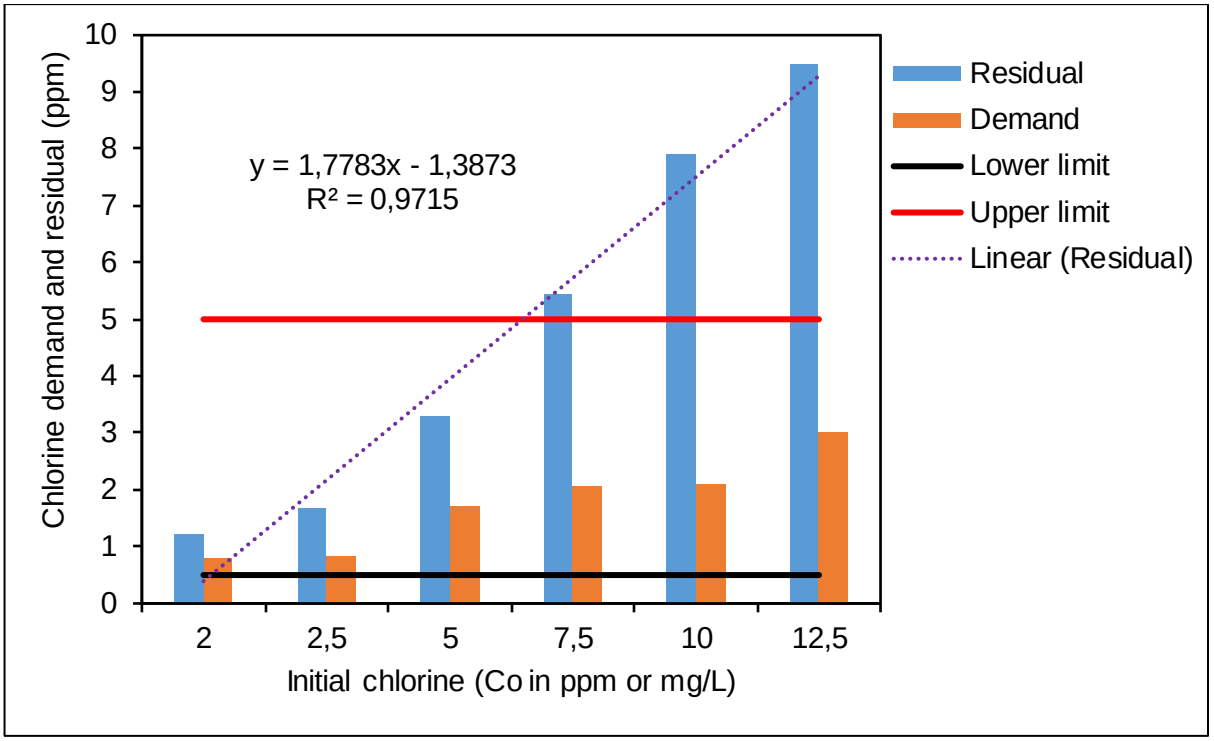

FIGURE 4.2: The effect of chlorine dosage on chlorine residual and chlorine demand for the final water in Vaalkop WTP (Conditions: varied concentrations, 10 minutes of mixing,100 rpm of mixing speed, and ambient temperature and pH)

As shown in Figure 4.2, the impact of chlorine concentration on residual chlorine and chlorine demand was thoroughly investigated. The chlorine demand of the final water at Vaalkop WTP was found to be low, which can be attributed to the quality of the raw water and the treatment processes applied. Specifically, it was observed that the chlorine residual increased as the chlorine concentration increased. The chlorine residual exceeded the chlorine demand at concentrations of 2 parts per million (ppm) or mg/L and higher, indicating that the consumption rate of chlorine by the final water is very low. This phenomenon can be influenced by various factors, including the chemical composition of the water source. To ensure both chlorine demand and sufficient residual chlorine levels to minimize the risk of water recontamination, an initial chlorine dosage of 5 mg/L or higher is recommended.

This dosage aligns with the limits defined by SANS 241-2 (0.5 mg/L to 5 mg/L). Considering these considerations, a chlorine dosage of 5 mg/L was determined to be the most effective post-chlorination dosage for the final water at Vaalkop WTP. However, further investigation and reporting are needed to determine the longevity of decontamination and the lifespan of chlorine within the water distribution system. The low chlorine demand indicates that the final water does not contain chlorine-hungry compounds, which can be attributed to the effectiveness of the water treatment system employed for raw water purification. It should be noted that chlorine-hungry compounds include organic matter (NOM), metals, ammonia, and other oxyanions, which can be considered as contaminants at elevated concentrations. (Xie et al., 2008, Warton et al., 2006, Van Haute et al., 2017, Tsai et al., 1992, Lytle and Liggett, 2016, Lu et al., 1999).

4.1.2. System Chlorine decay profiles for Vaalkop water distribution network.

The chlorine decay profiles of Vaalkop water distribution network are plotted on Figure 4.3 as shown below. The chlorine dosages were ranging from 2.5 to 20 mg/L for a period of 4500 minutes in a laboratory environment.

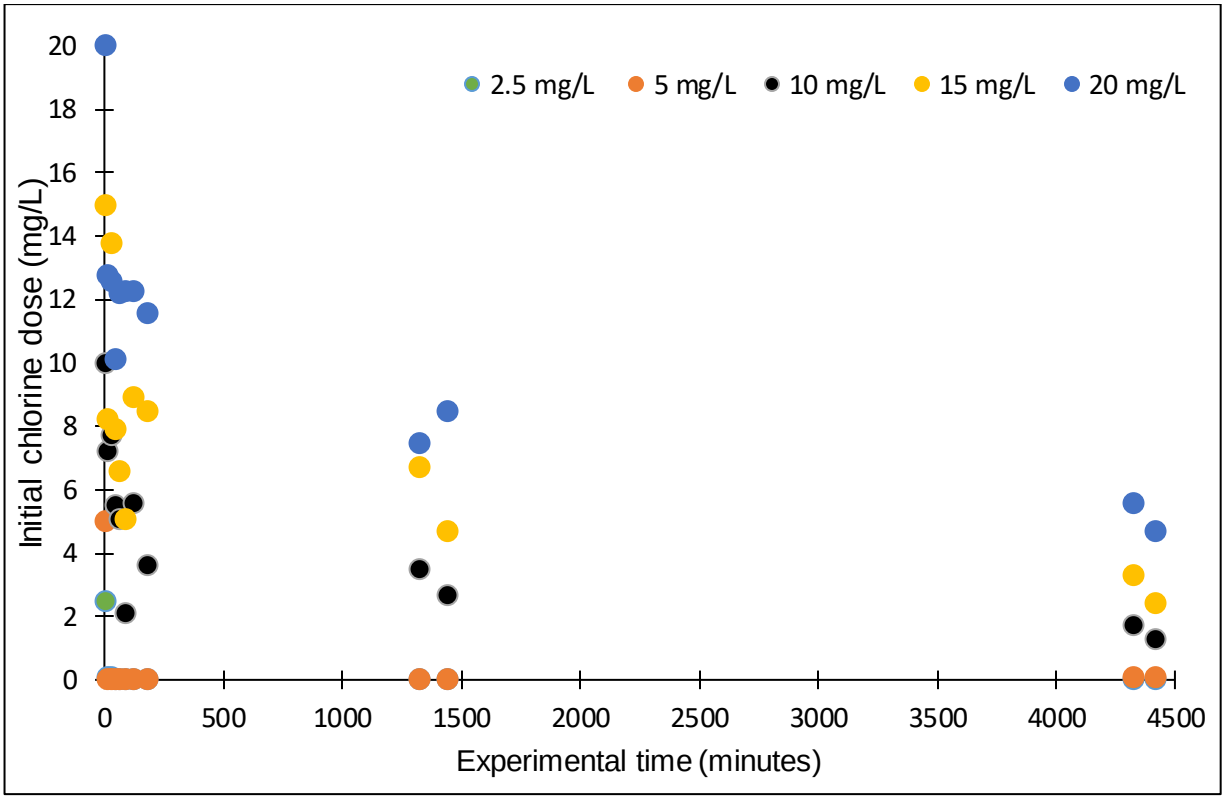

FIGURE 4.3: The experimented effect of chlorine dose with chlorine decay profiles at Vaalkop water distribution network with initial doses of (2.5-20) mg/L.

It could be seen from Figure 4.3, the study revealed that chlorine decay occurred within a few minutes of the reaction time. At an initial dose of 2.5 mg/L, chlorine decay was observed within 5 minutes of the reaction, indicating that all the chlorine in the water was consumed. This decay profile approached zero, suggesting that the chlorine dose was insufficient to react with all chlorine-reactive substances present. Similarly, at an initial dose of 5.0 mg/L, the decay profiles were like the 2.5 mg/L dose, indicating that the system's chlorine demand was not met, and the chlorine was rapidly depleted. These results did not comply with the recommended chlorine regulations outlined by the South African National water standards (SANS 241-2).

On the other hand, an initial chlorine dose of 10 mg/L was found to be sufficient, resulting in fast and slow decay phases. This indicated that the chlorine in the system met the chlorine demand, and an excess of chlorine was achieved. However, the chlorine levels increased from 2.1 to 3.2 mg/L at 180 minutes, which corresponded to the formation of disinfection by-products. Over time, these by-products reacted with the chlorine residual, leading to a reduction in chlorine levels to 1.31 mg/L at 4500 minutes. The initial dose of 15 mg/L followed a similar trend as the 10 mg/L dose, with the formation of disinfection by-products and a subsequent reduction to 2.42 mg/L. Similarly, the initial dose of 20 mg/L exhibited comparable decay profiles to the 10 and 15 mg/L doses. However, two phases of disinfection by-product formation were observed, with the first phase occurring between 90-180 minutes and the second phase between 1320-1440 minutes, resulting in a 1 mg/L increase in chlorine levels.

While the initial doses of 10, 15, and 20 mg/L managed to meet the system's chlorine demand, the chlorine residuals exceeded the recommended levels (SANS 241-2), and the formation of harmful by-products for human consumption should be avoided (Garcia-Avila et al., 2020, Goodarzi et al., 2020, Hua et al., 2015a, Li et al., 2013).

4.1.3. The effect of chlorine decay on water pH

The effect of chlorine decay with time towards the water pH has been investigated in this study and it is presented on Table 4.1.

TABLE 4.1: The effect of chlorine reaction to water pH for 2.5-20 mg/L.

Time (min)	2.5(mg/L)	5(mg/L)	10(mg/L)	15(mg/L)	20(mg/L)
15	6.61	6.76	7.08	7.45	7.78
30	7.31	7.4	7.47	7.79	7.91
45	6.81	7.2	7.36	7.64	7.77
60	6.98	7.1	7.38	7.54	7.74
90	7.33	7.39	7.46	7.58	7.71
120	7.21	7.31	7.51	7.66	7.79
180	7.19	7.32	7.39	7.55	7.69
1320	6.66	7.36	7.2	7.55	7.75
1440	7.09	7.24	7.35	7.46	7.54
4320	6.82	7.2	7.25	7.61	7.81
4419	7.27	7.35	7.58	7.7	7.85

The study found that the water pH during the reaction of chlorine with natural organic and inorganic matters, at an initial chlorine dose of 2.5 mg/L, ranged from 6.61 to 7.27 over a duration of 4419 minutes or 73.65 hours. However, for higher chlorine dose concentrations, the pH ranged from 7.78 to 7.85. It was observed that the reaction of chlorine with chlorine-reactive substances in the water did not have a significant impact on the water pH (Krishna et al., 2020, Zhang et al., 2017).

4.2. MATHEMATICAL MODELING OF FIRST AND SECOND ORDER CHLORINE DECAY MODELS.

The first order chlorine decay profiles are represented by the parallel first order (PFO) model, while the second order chlorine decay models are represented by the traditional second order model and the Quantitative Chlorine Reactive Substances (QCRS) model.

4.2.1. Determining the model reaction order of WDNS (Vaalkop)

The initial step in performing chlorine decay models is to determine the reaction order of the model. This can be achieved by linearizing the experimented data (chlorine residual) and plotting them against their corresponding time values as shown in Figure 4.4 below at 2.5 mg/L chlorine dosage.

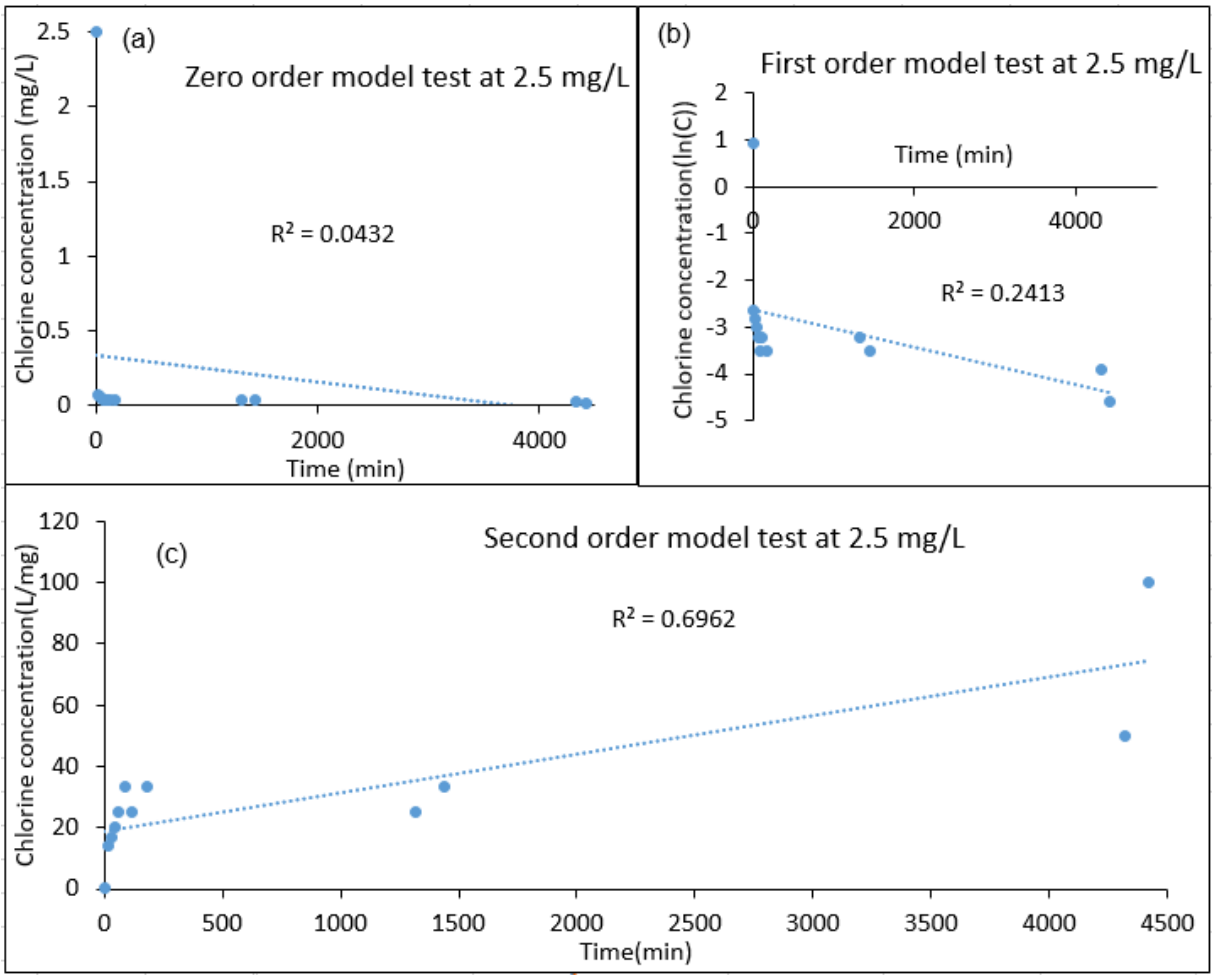

FIGURE 4.4: a) Zero order reaction model at 2.5 mg/L, b) First order reaction model at 2.5 mg/L and c) Second order reaction model at 2.5 mg/L.

Figure 4.4a depicts the plot of a zero-order model, and it is evident that the chlorine residuals do not follow a zero-order pattern, as indicated by a low linear correlation coefficient of 5%. In Figure 4.4b, the plot represents the linearized relationship between the natural logarithm of chlorine residual and time. It can be observed that

the relationship is not strongly linear, with a coefficient of determination of 34%. Figure 4.4c illustrates the relationship between chlorine residual and time for a second-order model. It is evident from the plot that the chlorine residual exhibits an inverse relationship with time for a chlorine dose of 2.5 mg/L, with a coefficient of determination of 89%.

The other plots of chlorine residuals from 5 mg/L to 20 mg/L has been summarized in Table 4.2 as shown below.

TABLE 4.2: The chlorine decay models from 5 mg/L to 20 mg/L

Chlorine dose (mg/L)	**Zero Order %**	**First order %**	**Second Order %**
5	0.0414	0.2652	0.728
10	0.658	0.8685	0.9465
15	0.4785	0.7243	0.8576
20	0.6043	0.8074	0.9161

For the chlorine dose of 5 mg/L, the chlorine residual data set showed a 4% correlation with the zero-order model, 27% correlation with the first-order model, and 73% correlation with the second-order model. However, for the chlorine dose of 10 mg/L, there was a strong correlation for all models. The zero-order model had a correlation of 66%, the first-order model had a correlation of 87%, and the second-order model had a correlation of 95%. It was observed that at lower chlorine doses below 10 mg/L, the chlorine demand is higher, and chlorine is consumed more rapidly, resulting in a second-order model. On the other hand, at chlorine doses above 10 mg/L, the chlorine demand is lower, leading to higher levels of chlorine

residuals and the presence of all three models. Overall, the results from chlorine decay models suggested the dominance of the second-order model due to the significant decay of the initial chlorine dose in all chlorine residual tests (Garcia-Avila et al., 2020, Gomes et al., 2016).

4. 2.2. The effect of Chlorine dose at chlorine decay modeling.

The effect of initial chlorine dose with time to describe chlorine decay models will be evaluated in this section from 2.5 to 20 mg/l.

The modeling of chlorine residual with the experimented results using the parallel first order model, second order model and Quantitative Chlorine reacting Substances (QCRS) model are being represented in Figure 4.5.

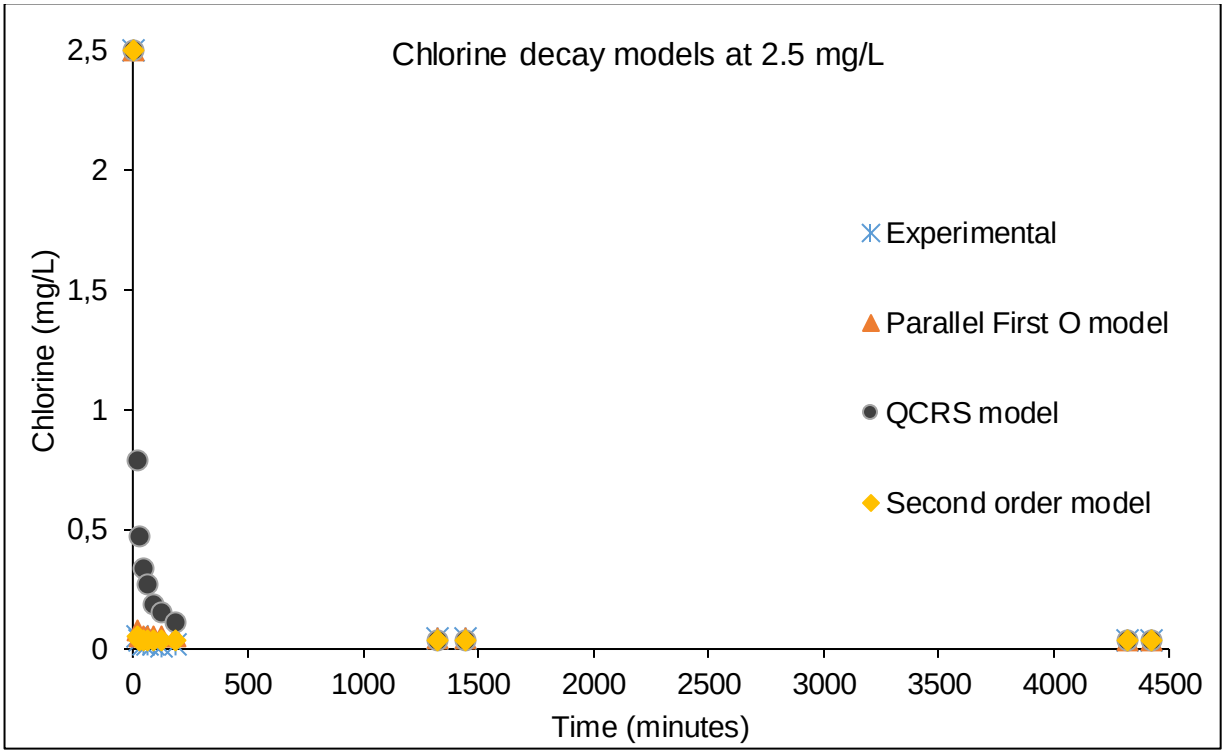

FIGURE 4.5: Chlorine decay at initial chlorine dose of 2.5 mg/L.

As shown in Figure 4.5, the rapid decay of chlorine observed within the first five minutes of reaction can be attributed to the high chlorine demand of the system.

When considering the initial chlorine dose of 2.5 mg/L, both the parallel first-order model (PFOM) and the second-order model closely matched the experimental data from 15 minutes to 4500 minutes, indicating that these models could effectively represent the experimental results with minimal error or deviation. However, the Quantitative Chlorine Reactive Substances (QCRS) model exhibited a lag above the experimental results within the first 200 minutes. After 1000 minutes, all the mathematical models and experimental results approached zero. The QCRS model relies on instantaneous and lasting chlorine decay phases, but for the initial dose of 2.5 mg/L, there was no lasting decay phase, and the model profile was higher than the experimental data.

The modeling of chlorine residual at an initial chlorine dose of 5 mg/L for the experimental results is presented in Figure 4.6. This figure showcases the application of the parallel first-order model, second-order model, and Quantitative Chlorine Reacting Substances (QCRS) model to represent the chlorine residual profiles.

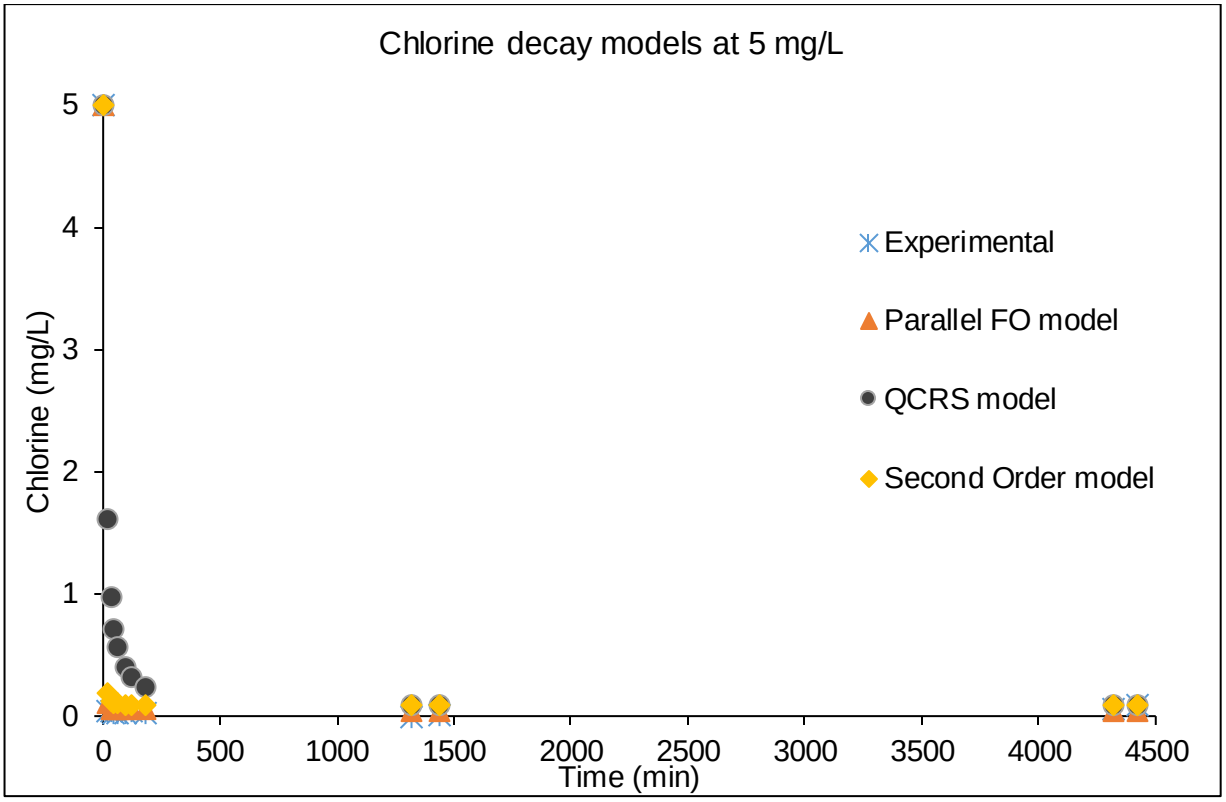

FIGURE 4.6: Chlorine decay at an initial chlorine dose of 5 mg/L

Figure 4.6 illustrates the chlorine decay profiles for the parallel first-order model, second-order model, and QCRS model at a chlorine dose of 5 mg/L. It is observed that due to the higher chlorine demand of the system, there is a rapid decay of chlorine. The parallel first-order model closely approximates the experimented chlorine residuals from 15 minutes to 4500 minutes. The second-order model is slightly above the experimental data throughout the reaction time. The QCRS model, on the other hand, exhibits a slower instantaneous decay rate within the first 200 minutes and is further above the experimented results.

Figure 4.7 depicts the modeling of chlorine residual at an initial chlorine dose of 10 mg/L using the parallel first-order model, second-order model, and QCRS model based on the experimented results.

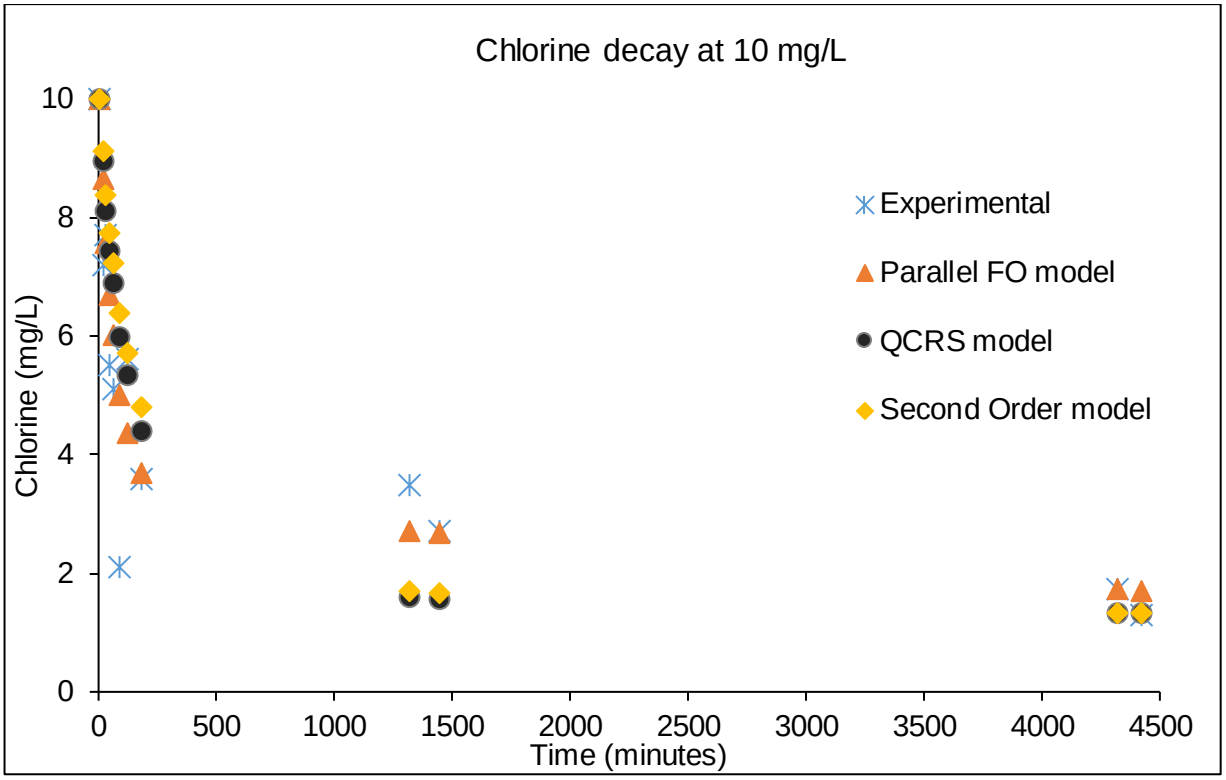

FIGURE 4.7: Chlorine decay modeling at an initial dose of 10 mg/L

In Figure 4.7, it can be observed that the chlorine demand of the system was lower at an initial chlorine dose of 10 mg/L, resulting in a relatively slower chlorine decay within the first 15 minutes of reaction time. However, there is an outlier in the experimental data at 200 minutes, indicating the presence of disinfection by-products (DBPs) that could not be accurately modeled by the mathematical models, which assume chlorine decay without an increase over time.

The parallel first-order model demonstrates a decay pattern that closely aligns with the experimented chlorine residuals from 15 minutes to 4500 minutes. The second-order model, on the other hand, slightly underestimates the experimented data throughout the reaction time. The QCRS model exhibits a steady chlorine decay rate within the first 200 minutes and is further below the experimented results. It should be noted that the QCRS model considers both instantaneous and lasting chlorine

decay phases, which may contribute to the differences observed between the model and experimental data. The effectiveness of the models improves as the initial chlorine concentration increases, as demonstrated by the plot for an initial dose of 10 mg/L in Figure 4.7. The rapid chlorine decay is not as instantaneous as observed for 2.5 and 5 mg/L doses due to the breakpoint of chlorination, and the chlorine demand of the system is achieved. As a result, an excess chlorine residual of above 1 mg/L is maintained at 4500 minutes, indicating a sufficient disinfection level.

The modeling of chlorine residual at an initial chlorine dose of 15 (mg/L) for the experimented results using the parallel first order model, second order model and Quantitative Chlorine reacting Substances (QCRS) model are being represented in Figure 4.8.

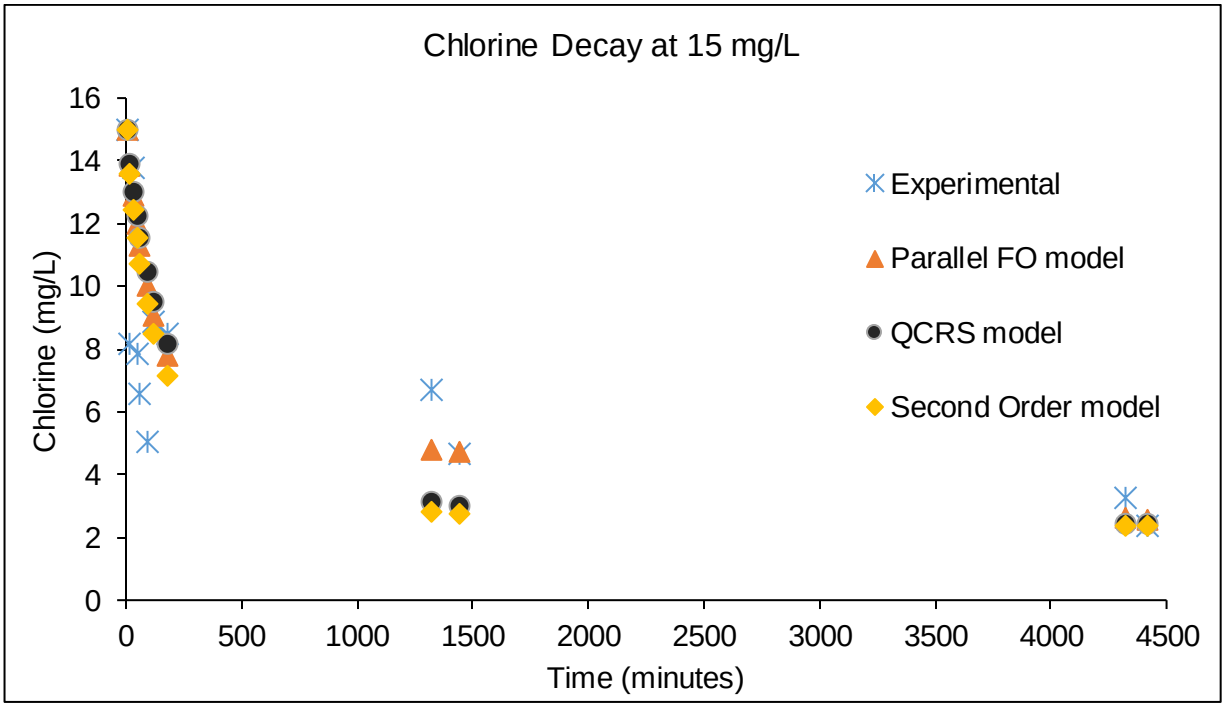

FIGURE 4.8: Chlorine decay modeling at an initial dose of 15 mg/L

The chlorine demand of the system was minimum hence the chlorine consumption was low initially. The parallel first order model was decaying relatively to the experimented chlorine residuals from 200 minutes to 4500 minutes while second order model was slightly below the experimented data throughout the reaction time and QCRS model was slightly above the experimented results with a steady chlorine decay rate within the 200 minutes. There were few outliers of the experimented results within the first 200 minutes of reaction time, this is the formation of DBP after meeting the chlorine demand of the system, however the DBP formation could not be mathematically modelled hence there was a deviation of trends within the first 250 minutes of reaction time.

The modeling of chlorine residual at an initial chlorine dose of 20 (mg/L) for the experimented results using the parallel first order model, second order model and Quantitative Chlorine reacting Substances (QCRS) model are being represented in Figure 4.9 as shown below.

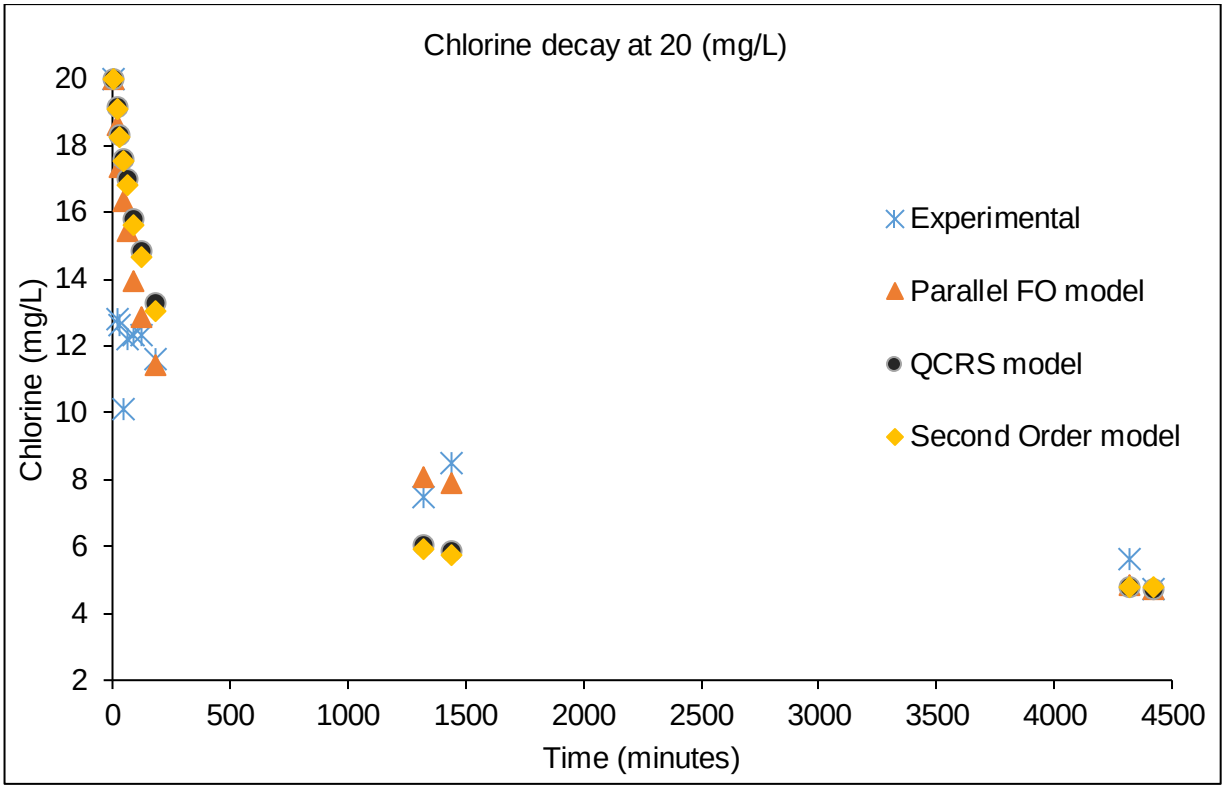

FIGURE 4.9: Chlorine decay modeling at an initial dose of 20 mg/L

As indicated in Figure 4.9, the PFO model decays relatively slower than the rapid chlorine decay of the experimental data within the 500 minutes of reaction time, however the PFO model was further decaying relatively to the experimented data and only few points were deviating from the experimented trend at 1500 minutes, this is because of DBP that was achieved within the 500 minutes of reaction time. The second order and QCRS model were decaying relatively close to each other while slightly deviating from the experimental data after 500 minutes.

4.2.3. The overall bulk chlorine decay rates with initial chlorine dose

The relationship of bulk chlorine decay rates with initial chlorine dose for all the mathematical models is illustrated in Figure 4.10.

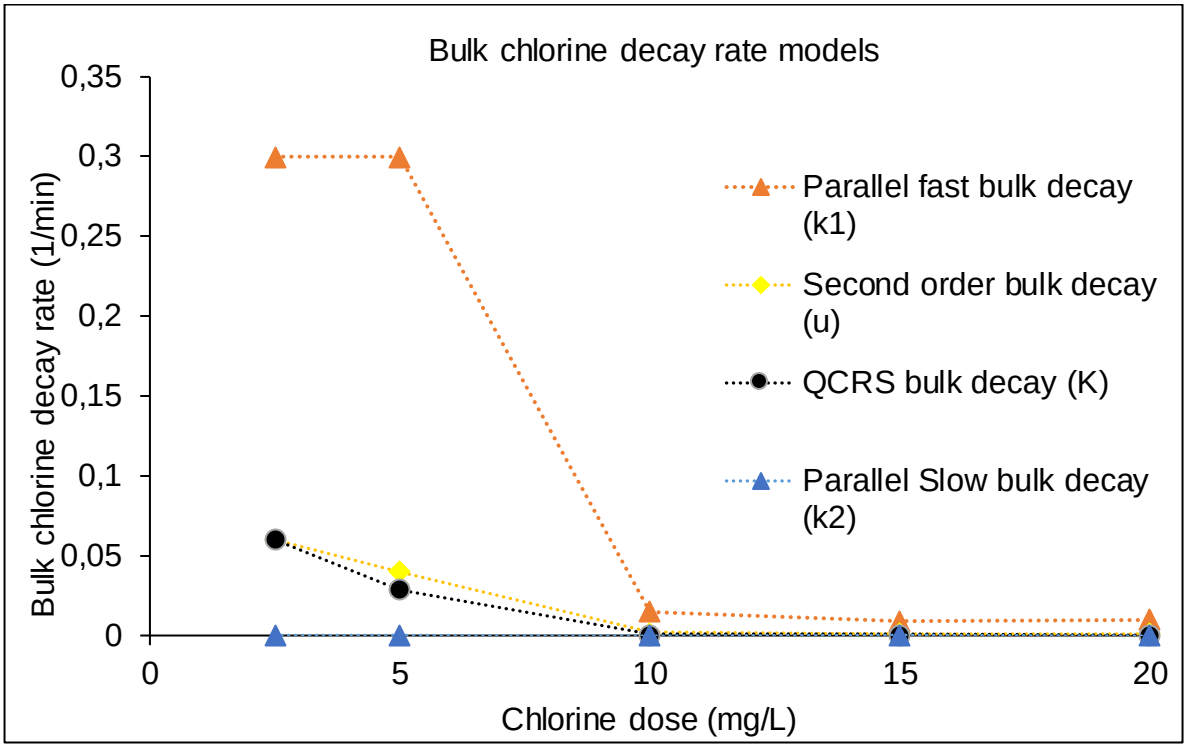

FIGURE 4.10: The bulk chlorine decay rate of the mathematical models with initial chlorine dose.

The parallel first order model in Figure 4.10 has two decay phases (fast and slow) as represented by k_1 and k_2 respectively. The parallel first order bulk decay rate in the fast phase (k_1) was found to be the highest at 0.3 (1/min) for chlorine dose of 2.5 and 5 mg/L respectively and further reduced to 0.002 (1/min) after initial chlorine dose of 10 - 20 mg/L, this was due to the chlorine demand being reduced at 10 mg/L, while the slow decay phase (k_2) was approaching zero in all chlorine dosages. The second order and QCRS model bulk decay rates were found to be 0.05 (1/min) at initial chlorine dose of 2.5 mg/L and further decreased parallel to 0.0001 (1/min)

at 20 mg/L (Fisher et al., 2017, Garcia-Avila et al., 2020, Goodarzi et al., 2020, Monteiro et al., 2015a, Sun et al., 2016, Tiruneh et al., 2019, Wang et al., 2019).

4.2.4. The linearized regression-based chlorine decay for second order, QCRS and PFO models.

The relationship of initial chlorine dose towards the second order bulk decay rate (min) is being determined in a linear form and is illustrated in Figure 4.11.

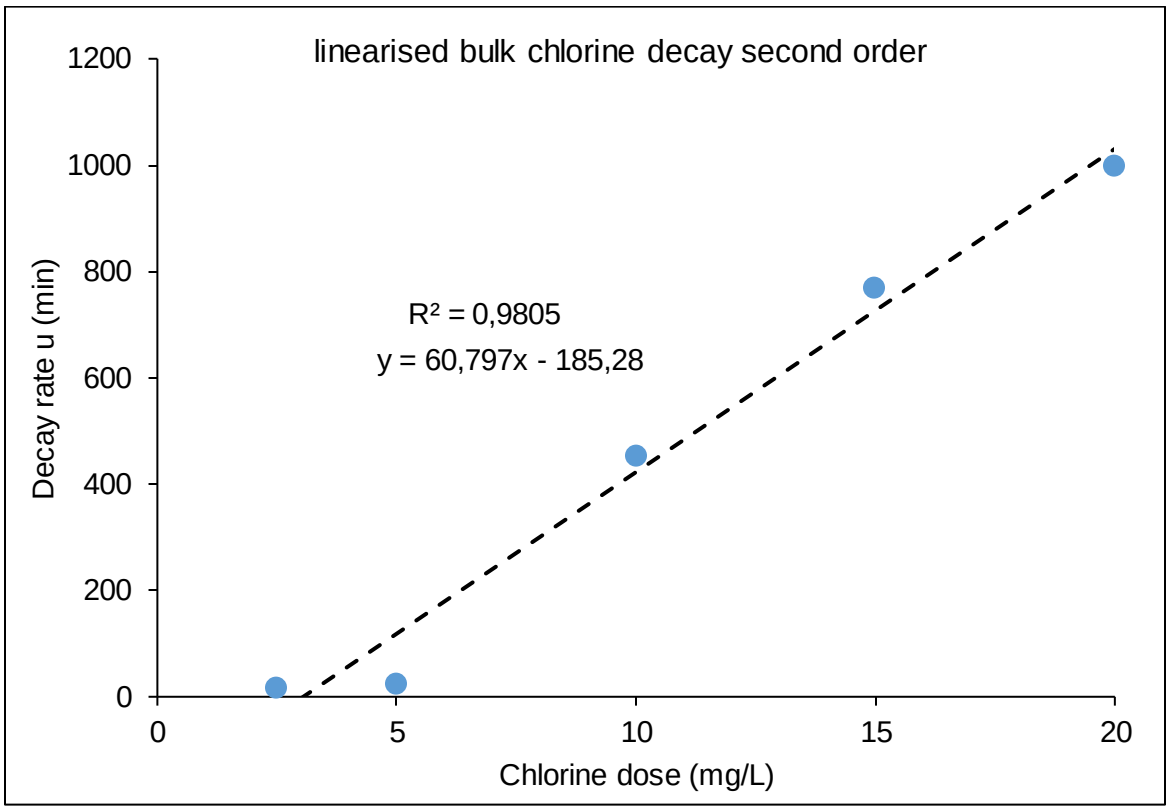

FIGURE 4.11: The linearized bulk chlorine decay rate with chlorine dose for second order model.

It could be seen from Figure 4.11 that the inverse bulk chlorine decay rate (1/u) is directly proportional to the change of initial chlorine dose by achieving a coefficient of determination of 98 %. This linear relationship implies that when chlorine dose increases so does the bulk decay rate decreases. However, the relationship is

based on the chlorine demand of the system hence the bulk decay rate of lower dosages was found to be constant hence the 98%.

The relationship of the linearized bulk chlorine decay rate with initial chlorine dose for Quantitative chlorine reacting substances (QCRS) model is being illustrated in Figure 4.12.

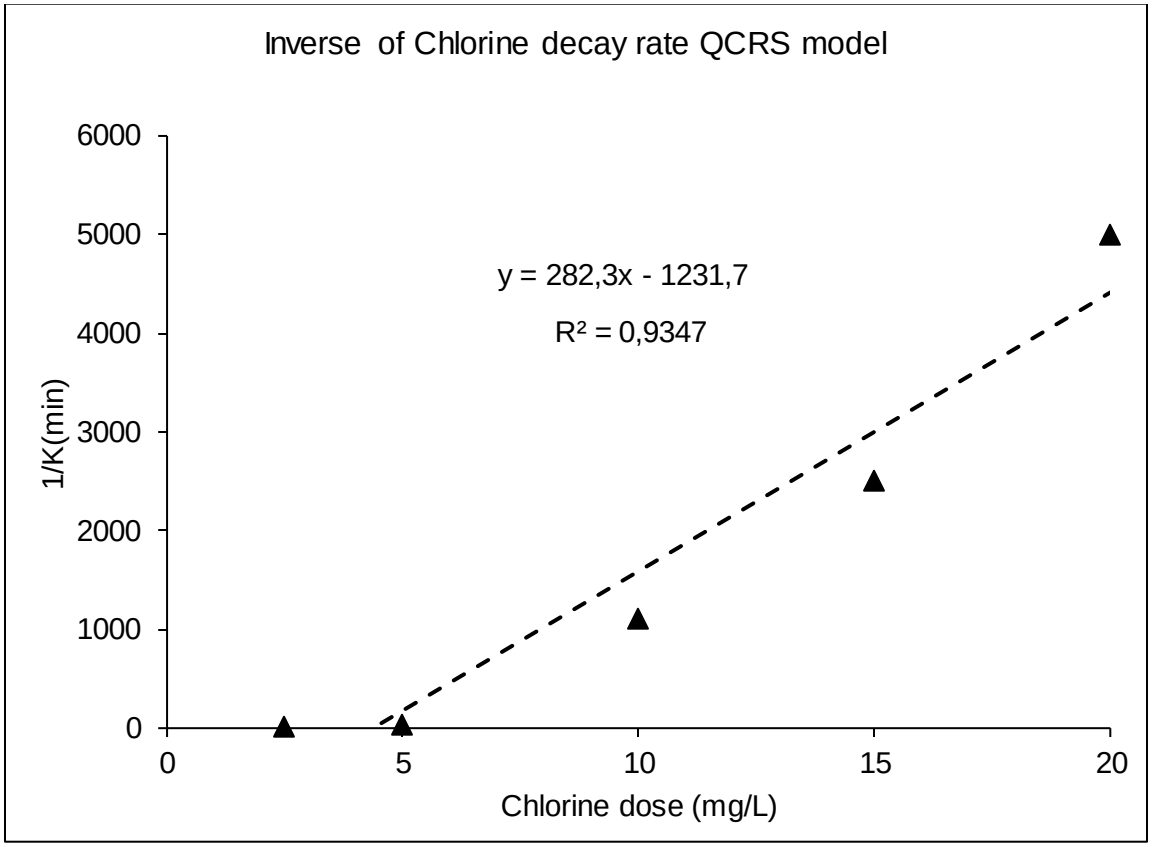

FIGURE 4.12: Linearized bulk chlorine decay with chlorine dose for QCRS model.

It could be seen from Figure 4.12 that the relationship of the two variables is linear at a coefficient of determination of 94%. The lower the initial chlorine dose the lower the bulk decay rate (min) and as the chlorine dose increases so does the bulk decay rate (min) increases. However further calibration to improve the relationship is required.

The relationship of parallel firs order model bulk decay rate in the fast decay phase ($1/k_1$) with chlorine dose is being illustrated in Figure 4.13.

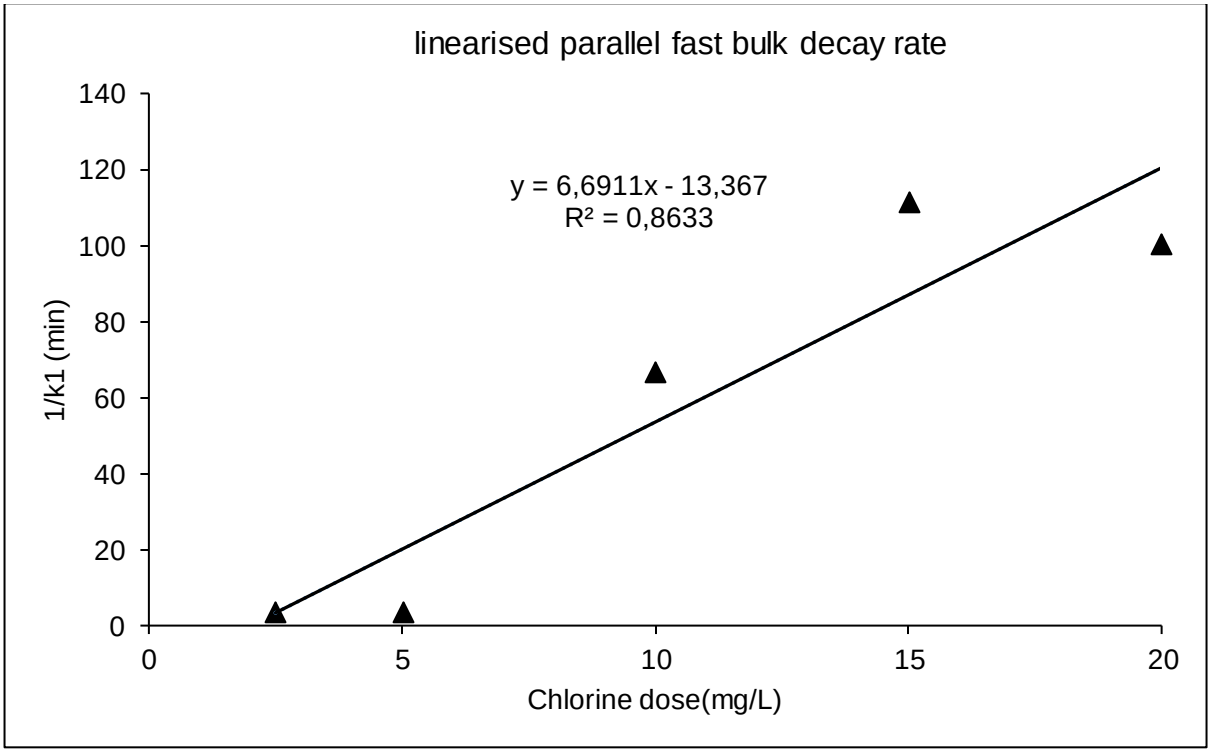

FIGURE 4.13.The linearized bulk chlorine decay with chlorine dose for parallel first order model (fast phase).

It could be seen from Figure 4.13 that the inverse bulk decay rate ($1/k_1$) is linear with a coefficient of determination of 86.3 %. The lower initial chlorine had a constant bulk decay rate and when the chlorine dose increased to 10 mg/L the bulk decay rate increased to 62 (min) while the at 15 mg/L the bulk decay rate was at 115 (min) and further decreased to 90 (min) at 20 mg/L. This particular trend is not linearly increasing with increase in chlorine dose hence the coefficient of determination was 86 %.

The relationship of parallel firs order model bulk decay rate in the slow decay phase ($1/k_2$) with chlorine dose is being illustrated in Figure 4.14.

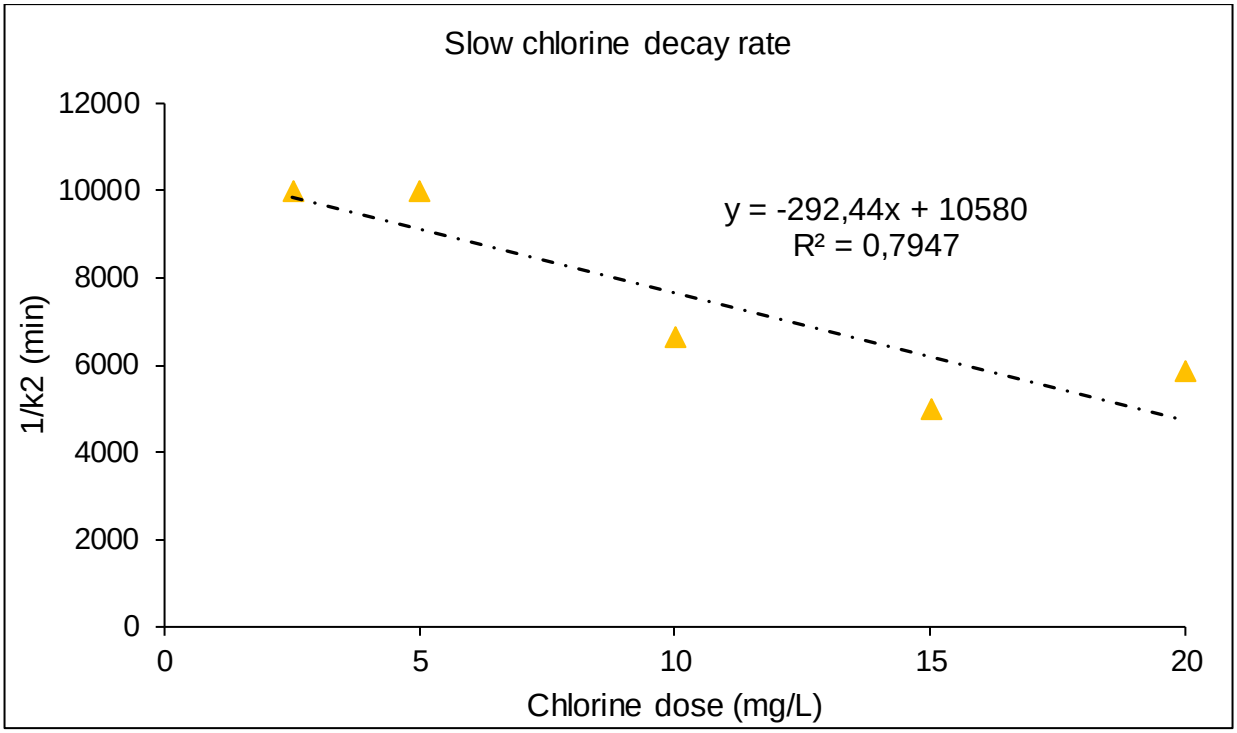

FIGURE 4.14. The llinearized bulk chlorine decay with chlorine dose for parallel first order model (fast phase).

The linearized relationship was linearly descending with an increase in chlorine dose and have attained a coefficient of determination of 80 %. It could be seen that the trend in Figure 4.14 is not linear sufficient, since well it started from 10, 000 (min) at 2.5-5 mg/L, declined to 500 (min) at 15 mg/L and further inclined to 600 (min) at 20 mg/L (Cong et al., 2012, Fisher et al., 2017, Garcia-Avila et al., 2020, Goodarzi et al., 2020, Monteiro et al., 2015a, Sun et al., 2016, Tiruneh et al., 2019, Wang et al., 2019).

4.2.5. The linearized chlorine decay modeling parameters with initial chlorine dose

The modeling parameters for second order (R), parallel first order (x) and QCRS (Q) are being investigated with the effect of initial chlorine dose as shown in the Figure 4.15.

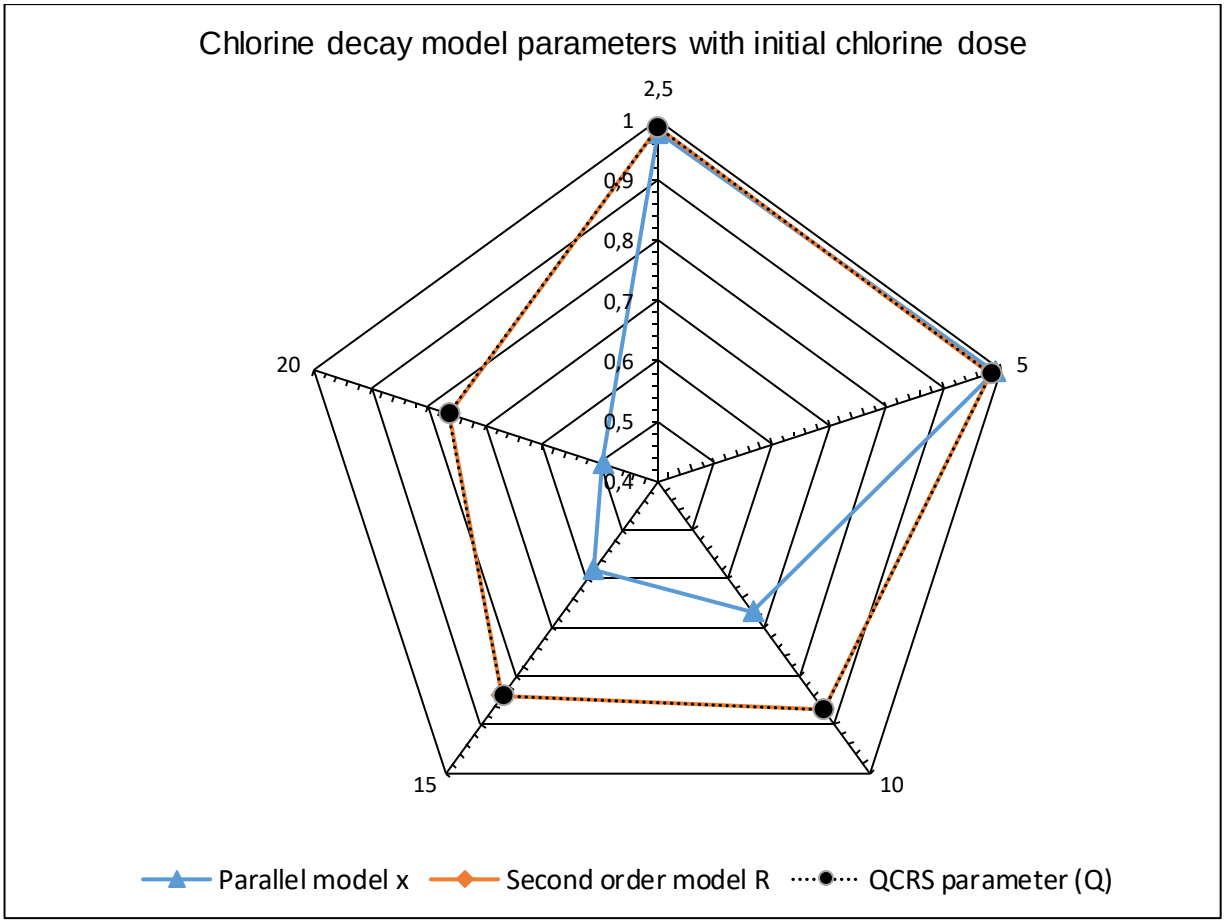

FIGURE 4.15. The chlorine decay modeling parameters with initial chlorine dose

All three modeling parameters (x, R and Q) for initial chlorine dose of 2.5 -5mg/L were found to be above 98%, this is because of the high chlorine demand of the system. However, as the initial chlorine dose increases from 10 – 20 mg/L the model parameter x decreased from 65 to 50% respectively, this is because of chlorine demand being reduced in the system. The model parameters for the second order and QCRS model have maintained constant decrement at every initial chlorine dose, and at initial chlorine dose of 10-20 mg/L the QCRS and second order model has reduced from 87 to 77% respectively. This is because the QCRS model was reduced to second order models since the driving forces (instantaneous and lasting chlorine decay phase) were not present. The second order chlorine decay model is a double

element modeling technique that accommodate the reaction of chlorine with chlorine reactive substances through an irreversible reaction , while parallel first order model assume that chlorine reacts with a single reactant and chlorine is a limiting reagent in both slow and fast chlorine decay phases (Tiruneh et al., 2019, Wang et al., 2019).

4. 3. COMPUTATIONAL FLUID DYNAMICS OF SOLUTE TRANSPORT AND WATER QUALITY FOR CHLORINE DECAY MODELS.

The developed mathematical first and second order chlorine decay profiles were simulated into solute transport and water quality models to determine the variation or similarity of chlorine dose with distance.

4. 3.1. Simulation temporal variation in residual chlorine concentration using COMSOL Multiphysics.

4. 3.1.1. The first order model of chlorine decay using COMSOL Multiphysics in water distribution network.

The first order simulation of temporal chlorine residual concentration with distance as a function of initial chlorine concentration at 5 mg/L is shown in Figure 4.16: a). The relationship of initial chlorine against distance is illustrated on Figure 4.16(a-d).

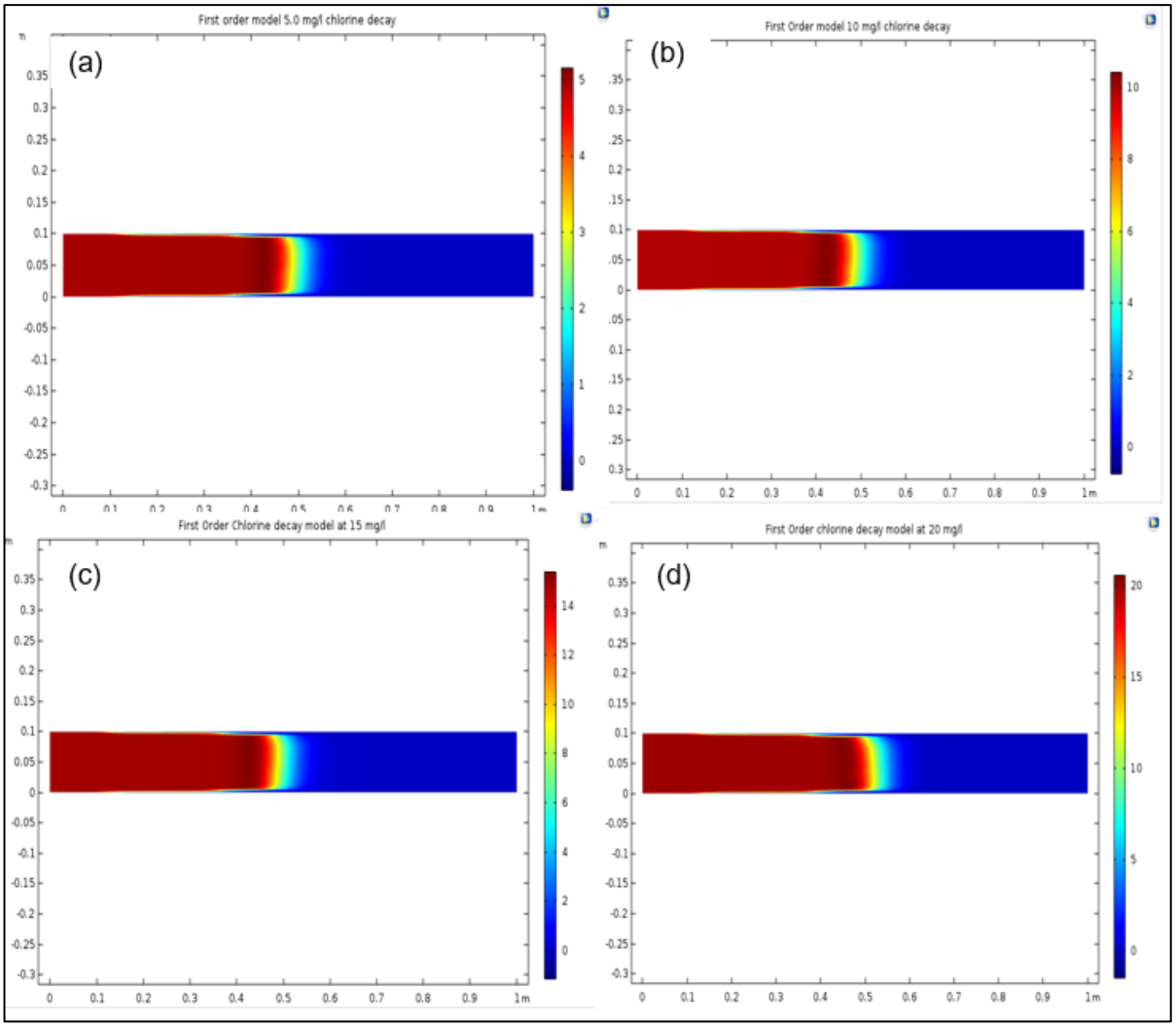

FIGURE 4.16: :(a-d) The simulation of First order model temporal variation of chlorine residual with distance using COMSOL Multiphysics from 5 to 20 (mg/L) chlorine dose.

It was observed that at a range of 0.2 m from Figure 4.16 a), the initial chlorine decay was established as it decayed from 5 mg/L as shown in the red colorings of the results, the chlorine was further consumed to 1.5 mg/L at 0.5 m as indicated by the rainbow coloration at the midpoint of the blue and red color. The final chlorine residuals in the system were approximating to zero at the end points of the system as indicated by the dark blue color. In the beginning, initial concentration of chlorine was observed to decrease rapidly, and this could be attributed to high chlorine demand in the final water produced in the plant. Similar observations were recorded

for 10, 15 and 20 mg/L chlorine concentrations as shown in Figure 4.16: (b, c, and d) respectively.

4. 3.1.2. The simulation of Second order model of chlorine decay using COMSOL Multiphysics in water distribution network.

The second order simulation of temporal chlorine residual concentration with distance as a function of initial chlorine concentration of 5 to 20 mg/L is shown in Figure 4.17(a-d).

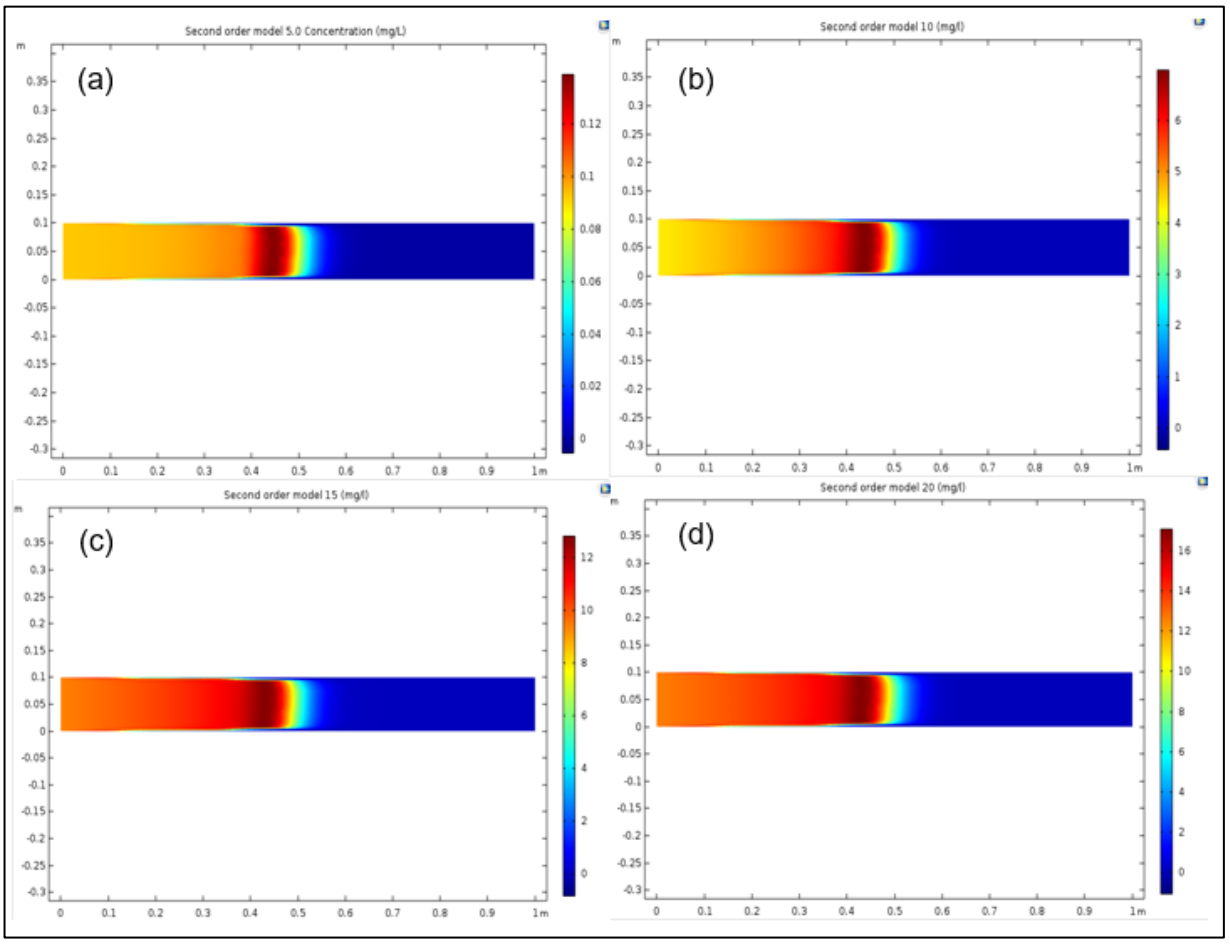

FIGURE 4.17: The simulation of second order model temporal variation of chlorine residual with distance using COMSOL Multiphysics from 5 to 20 (mg/l) chlorine dose.

The relationship of initial chlorine against distance is illustrated in Figure 4.17. It was observed that at a range of 0.2 m from Figure 4.17.a, the initial chlorine decay was very rapid, and the lasting chlorine decay was established from 0.12 to 0.10 mg/L as shown in the dark yellow color between 0 and 0.38 m. The chlorine was further consumed to 0.08 mg/L at 0.5 m as indicated by the rainbow coloration at the midpoint of the blue and dark red color. The final chlorine residuals in the system were approximating to zero at the end points of the system as indicated by the dark blue color. In the beginning, initial concentration of chlorine was observed to decrease rapidly, and this could be attributed to high chlorine demand in the final water produced in the plant. Similar observations were recorded for 10, 15 and 20 mg/L chlorine concentrations as shown in Figure 4.17, b, 4.17: c, and 4.17: d respectively (Goodarzi et al., 2020, Hoai and Hoang, 2017).

4. 3.2. Simulation temporal variation in residual chlorine concentration using EPANET software.

4. 3.2.1. The simulated first order chlorine decay model using EPANET software.

The concentration of free chlorine (residual chlorine) as a function of initial concentration for first order chlorine decay model in different nodes of water distribution are shown in Figure 4.18.

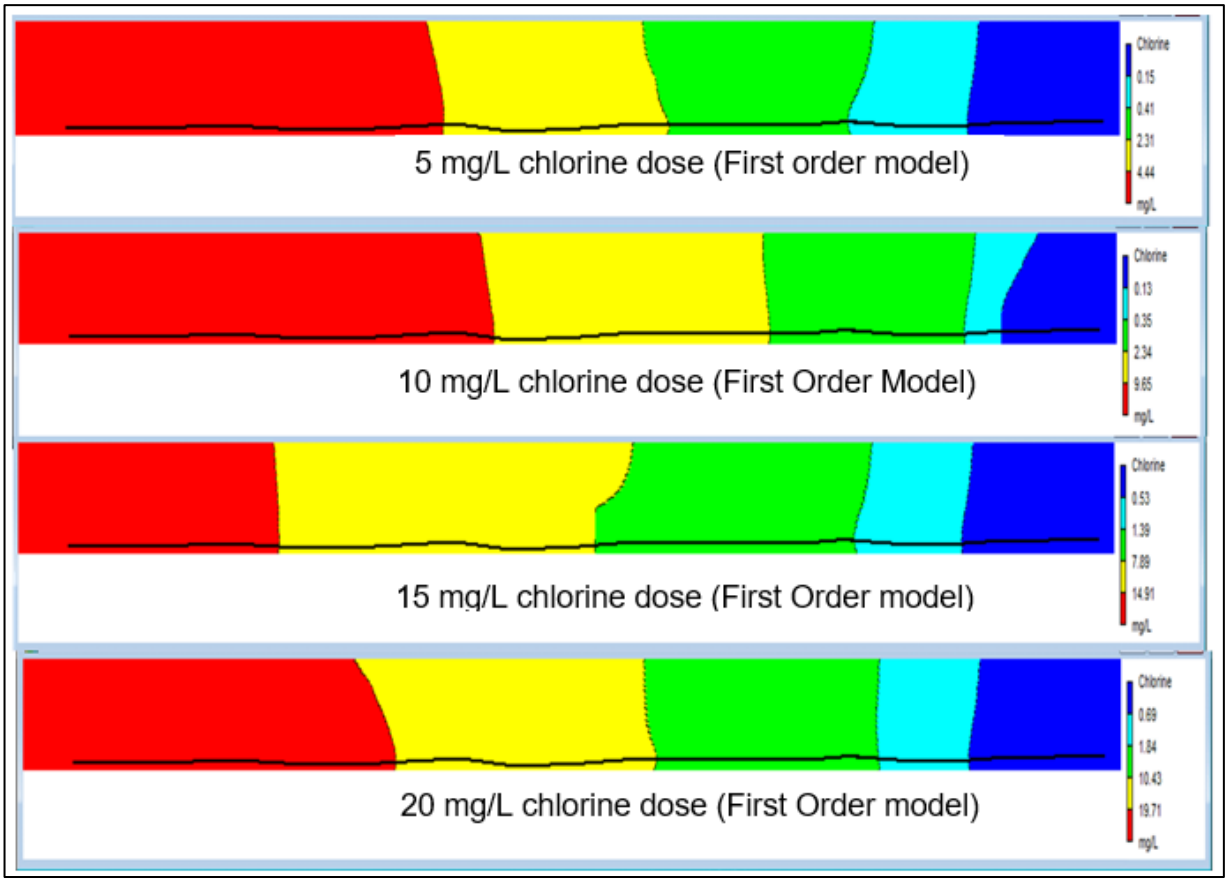

FIGURE 4.18: The first order chlorine decay model contour plots for chlorine decay and its respective residual and initial concentration in the water distribution network.

The red area shown on Figure 4.18 represents the high concentration of chlorine that further decays rapidly to a minimum concentration in the yellow region. The green region illustrates the lower concentration as the decay rate proceeds to the blue region where the chlorine concentration is at the lowest. For the 5 mg/L, chlorine decay is being established between 14 km to a lower concentration of 2.31 mg/L as highlighted in the yellow region. As chlorine residuals move further towards the end points, the chlorine remaining in the system was found to be below 0.8 mg/L. The observations were similar for 10, 15 and 20 mg/L. It was observed that a higher initial dose of chlorine resulted in a higher chlorine residual, while the lower the initial chlorine dose the lower the chlorine residuals. This result may be because water flow rates are reduced or increased during the hours of lower consumption or higher

consumption, thus, increasing the chlorine decay constant and accelerating the decay of the disinfectant in the pipeline or reservoir.

4.3.2.2. The simulated second order chlorine decay model using EPANET software.

The simulated second order chlorine decay in a water distribution system using EPANET is presented in Figure 4.19.

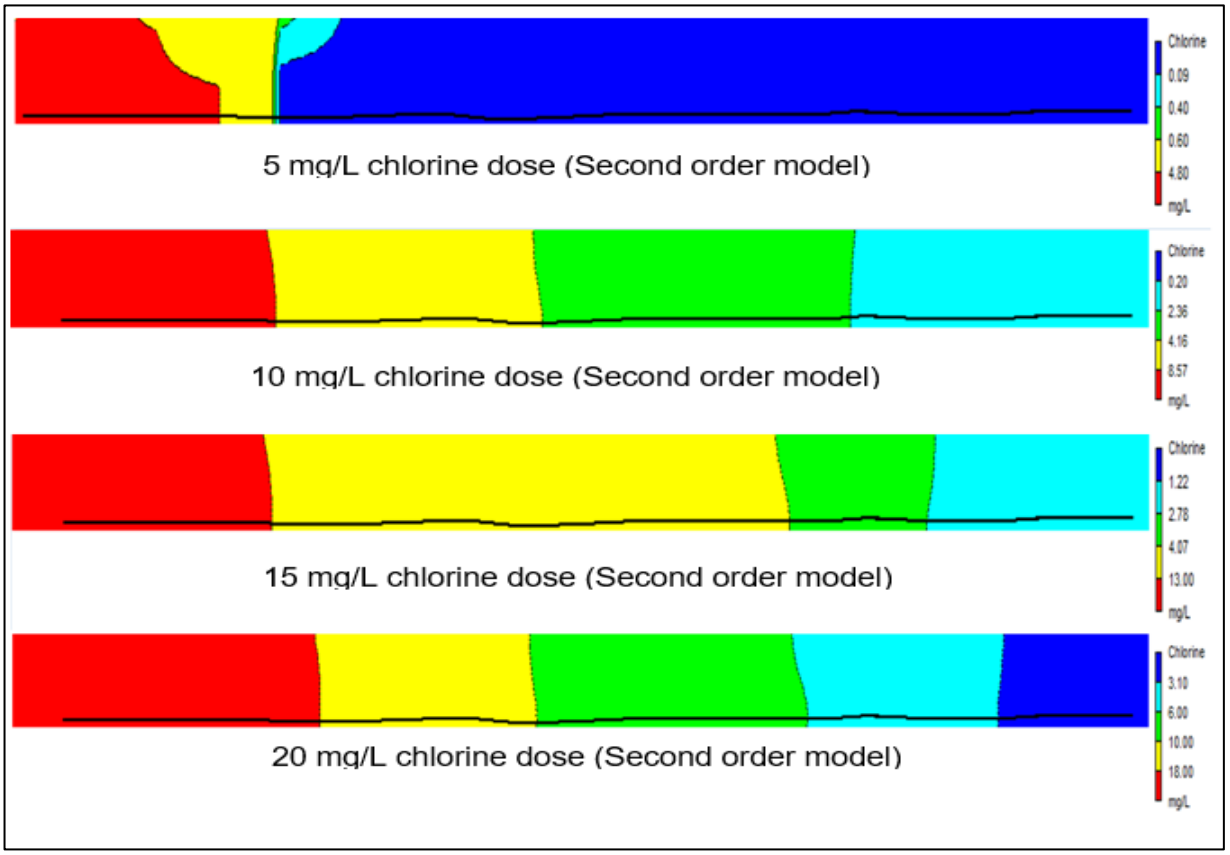

FIGURE 4.19: The Second order chlorine decay model contour plots for chlorine decay and its respective residual and initial concentration in the water distribution network.

The top contour in Figure 4.19 illustrates the chlorine decay with an initial dose of 5 mg/L and the bottom contour plot illustrates the chlorine decay for 20 mg/L. The chlorine decay of 5 mg/l chlorine dose has shown a rapid decrease within 15 km of the distribution as it decayed from 4.80 mg/L as shown by the red color to 0.60 mg/L as indicated by the yellow color, it further decayed from 0.60 to 0.40 mg/L as

indicated by the green color and the lasting chlorine decay was established from 0.09 mg/L to approximately 0 mg/L from 30 km to the end point of the system. Similar chlorine decay temporal profiles have been observed for 10, 15 and 20 mg/L while the total chlorine residual at the end points were found to be 0.20, 1.22 and 3.10 mg/L respectively. This indicated that second order chlorine decay model could establish a higher chlorine residual for a longer period (Monteiro et al., 2014., Nono et al., 2018, Van der Walt et al., 2021).

4. 4. MODEL VALIDATION

The developed mathematical and simulated chlorine decay models were validated by using the available literature for quality purposes.

4.4.1. Validating mathematical models.

Table 4.3 summarizes the comparison of the data that was found in this project and the other researcher's findings. The proposed first order model of the study was guided through the work of Tiruneh et al. (2019), however the reaction rate bulk coefficient was performed hourly while in this project a time scale of minutes was used.

TABLE 4.3 Validating the first order model of initial chlorine dosage at various concentration for this study.

This study		**(Tiruneh et al., 2019))**		**(Garcia-Avila et al., 2020)**		**(Angelouds A, 2014)**	
Initial Cl2	Kb(1/min)	Initial Cl2	Kb (1/h)	**Initial Cl2**	Kb(1/min)	Initial Cl2	Kb (1/h)
2.5	0.0012	0.77	0.15	**2.5**	0.0012	0.77	0.15
5	0.00109	3.88	0.07	**5**	0.00109	3.88	0.07
10	0.00045	6.59	0.037	**10**	0.00045	6.59	0.037
15	0.0004	18.38	0.019	**15**	0.0004	18.38	0.019
20	0.00032	-	-	**20**	0.00032	-	-

The study produced similar results as compared to other sources, since well the bulk reaction rate coefficient was found to be higher at higher concentrations from 0.0012 (mg/L.min) and as the dose increases so does the bulk decay rate decreases to 0.00032 (mg/L.min). This is being observed also in the literature as summarized in Table 4.3.

4.4.2. Validating COMSOL Multiphysics results

The first order model of initial chlorine dosage at various concentrations for this project and compared to another researcher's work has been presented on Table 4.4.

TABLE 4.4:First order model of chlorine decay for this study and the study done by Goodarzi et al. (2020).

This study			**(Goodarzi et al., 2020)**		
Inlet Cl_2 concentration	Final Concentration(mg/l)	Chlorine decay %	Inlet Cl_2 concentration(mg/l)	Final Concentration	Chlorine decay %
2.5	0.01	99.6	2.0	1.26	38
5	0.02	99.6	-	-	-
10	1,5	85	-	-	-
15	2,4	84	-	-	-
20	4.7	76.5	-	-	-

The control modelling parameters of chlorine decay for the current study has been the initial dose with respect to time. The chlorine decay for the simulated chlorine temporal residuals has been found to be established from 2.5 to 0.01 mg/L resulting in a 99.9 % of chlorine demand while Goodarzi et al. (2020) found a total chlorine residual of 1.26 mg/L having a total chlorine demand of 38 %. The chlorine demand and decay of this study was found to be the highest as compared to another research.

4.4.3. Validating EPANET results.

The first order model of initial chlorine dosage at various concentrations for this project and compared to another researcher's work using EPANET software has been presented on Table 4.5.

TABLE 4.5: The first order model of initial chlorine dose at various concentration for EPANET software model validation.

Parameters	This study	(Monteiro et al., 2014.)	(Nono et al., 2018)
Temperature	20 °C	20 °C	20 °C
Initial chlorine dose	2.5 mg/l	0.5 – 0.75 mg/l	2.5
Bulk decay	0.0012 (1/min)	0.045 (1/h)	0.037 (1/h)
Model Order	First Order Model	First Order Model	First order model
Distance	70 Km	23 Km	N/A

In this study for initial chlorine dose of 2.5 mg/L first order model, the bulk chlorine decay coefficient was found to be at 0.0012 (1/min) for a simulated water distribution network that is 70 long km using EPANET software while has found the bulk decay coefficient to be at 0.045 (1/h) for a chlorine dose of 0.5-0.75 mg/L in a 23 km water distribution network and water distribution network while other researchers have found Nono et al. (2018).

4. 5. OPTIMIZING THE VAALKOP WATER DISTRIBUTION SYSTEM

The sole purpose of performing chlorine decay assays and model is to optimize the system at study. This section will showcase the steps in determining and simulating the optimum chlorine dosage.

4. 5.1. Breakpoint chlorination

The breakpoint chlorination of Vaalkop water distribution system is being illustrated by Figure 4.20.

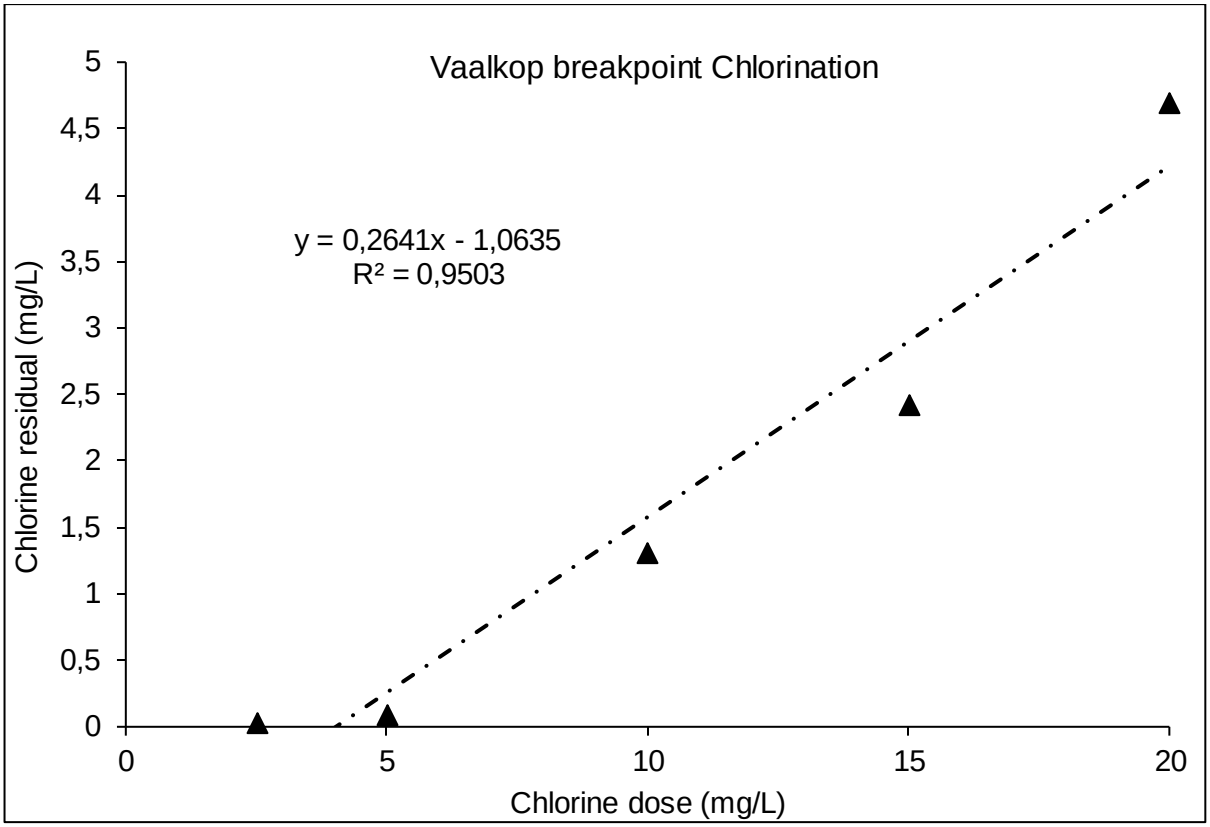

FIGURE 4.20: The breakpoint chlorination of Vaalkop water distribution system

The relationship of chlorine residual with chlorine dose is plotted as illustrated by Figure 4.20, it could be seen that the chlorine residual was linearly dependent to the chlorine dose of the system having 95 % coefficient of determination. The chlorine residual of 2.5 and 5.0 mg/L were almost the same at 0.03 and 0.09 mg/L respectively and it could be seen that as chlorine dose increases to 20 mg/L so does the chlorine residual increases to 4.7 mg/L. This relationship can be used to predict the chlorine dose at any given point by choosing the chlorine residual that will be efficient to control the regrowth of pathogens in the system. The recommended chlorine residual was chosen to be 0.6 mg/L and the calculated chlorine dose was found to be 6.30 mg/L with 95% confidence.

4. 5.2. Chlorine demand and chlorine dose

The chlorine demand of the Vaalkop water distribution system is plotted with the initial chlorine dose as presented in Figure 4.21.

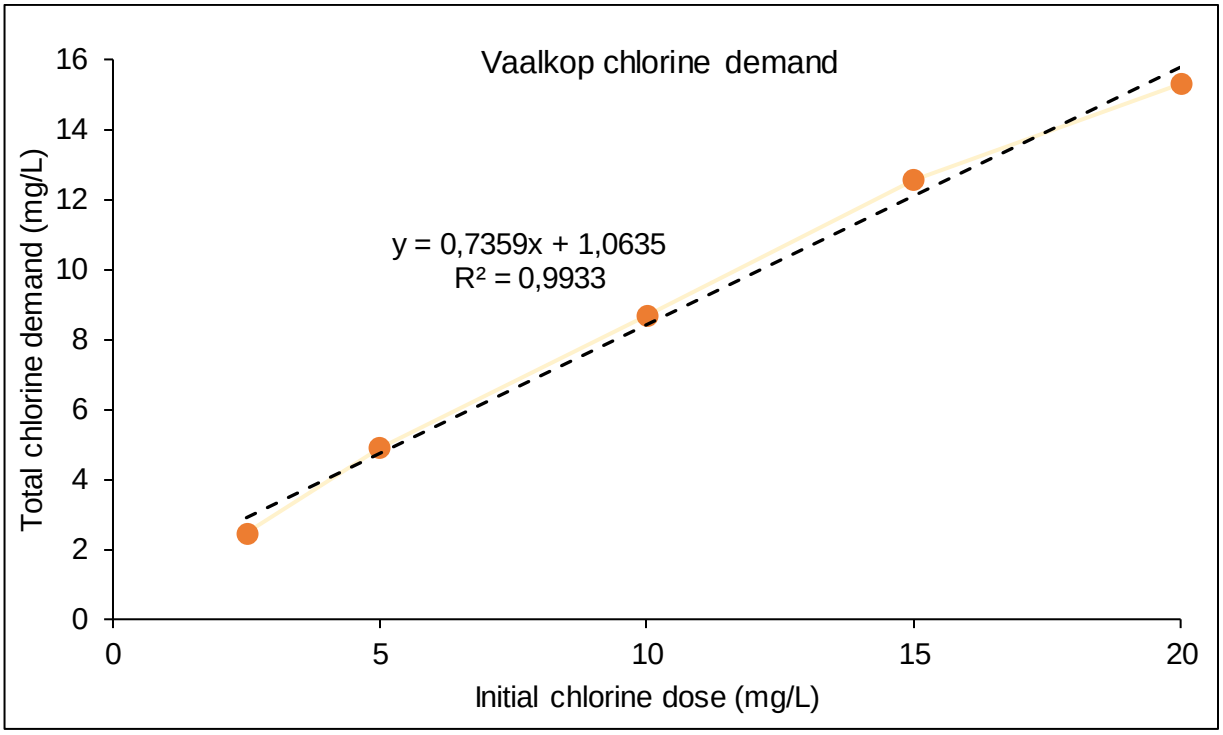

FIGURE 4.21: The total chlorine demand of the water distribution system with the initial chlorine dose

The relationship of chlorine demand with initial chlorine dose is linear with a 99.3 % coefficient of determination. It could be seen from the Figure 4.21 that at an initial chlorine dose the total chlorine demand of the system was at 2.47 mg/L implying that the chlorine dose was almost consumed since well the chlorine demand was high and at an initial chlorine dose of 10 mg/L the chlorine demand was at 8.7 mg/L. The relationship of chlorine demand with chlorine dose was used to calculate and predict the chlorine demand of the water distribution system when the initial chlorine dose was set to be 6.30 mg/L, it was found that the calculated chlorine demand would be 5.71 mg/L with 99.3 % confidence.

4. 5.3. Optimized Chlorine decay second order model

The two chlorine reactive components (Second Order Model) have yielded the best chlorine decay profiles; hence it is used to represent the modeling of optimum dosage.

The recommended chlorine dose of 6.30 mg/L as predicted by the breakpoint chlorination and chlorine demand was then used to calculate the chlorine decay second order model of the system as shown in Figure 4.22.

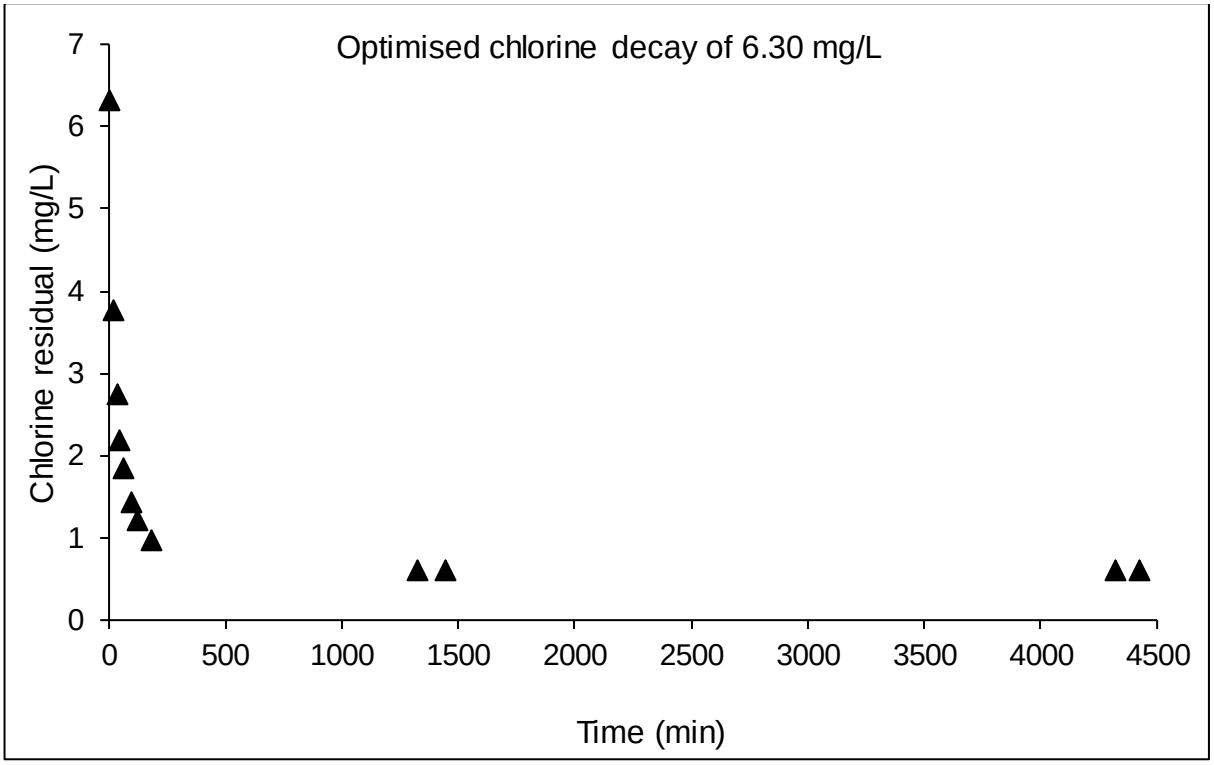

FIGURE 4.22: The optimized second order chlorine decay model.

It could be seen from Figure 4.22 that chlorine decays rapidly from 6.30 mg/L to 0.8 mg/L within the first 200 min and the lasting chlorine decay was from 0.8 to 0.60 mg/L from 200 minutes to 4500 minutes. The plot represents and predicts the results that will be found when analyzing the chlorine dose of 6.30 mg/L in the laboratory.

This will further improve the optimizing techniques within the water distribution system.

4. 5.4. The optimized chlorine decay simulations COMSOL Multiphysics and EPANET.

The optimized chlorine decay second order model was then simulated in COMSOL Multiphysics and EPANET software to predict the chlorine decay within the distribution system and the results were plotted in Figure 4.23a,nd b, for COMSOL and EPANET respectively.

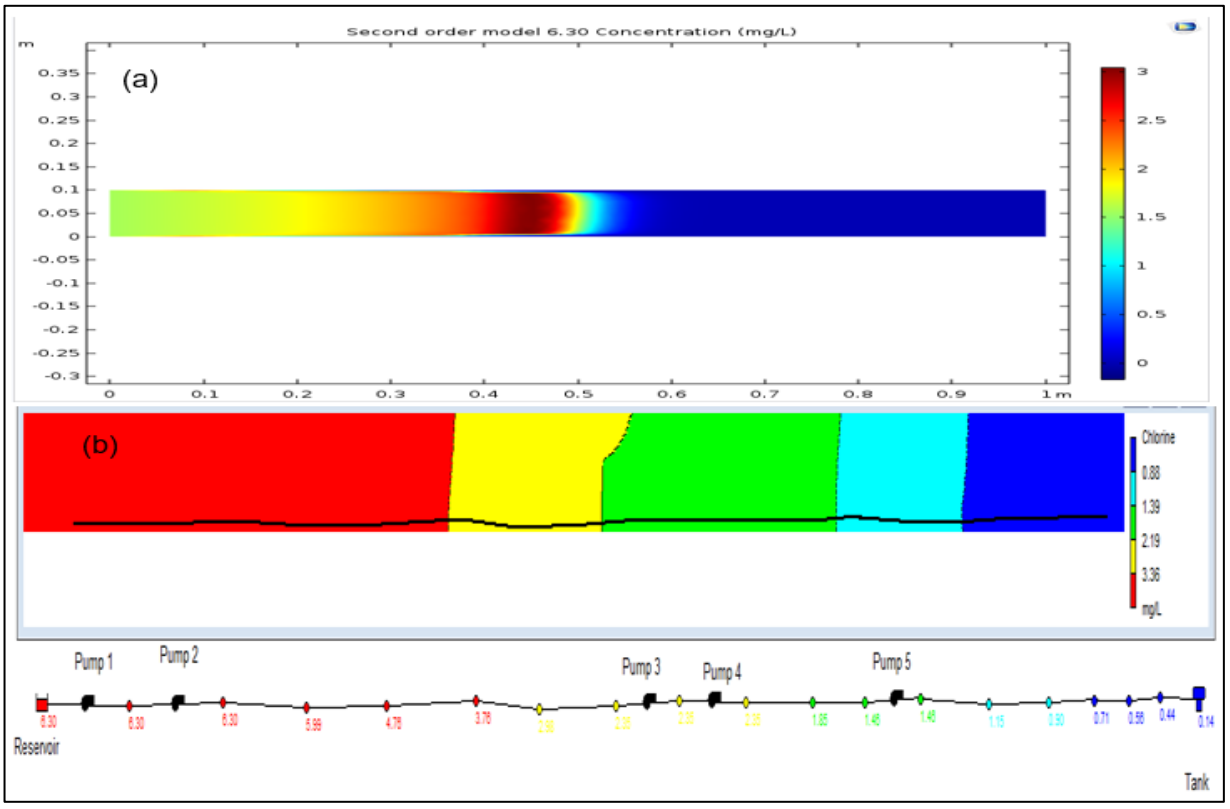

FIGURE 4.23: The Simulation of the optimized second order chlorine decay at initial chlorine dose of 6.30 mg/L, a) Solute transport model and b) Water quality model.

The chlorine decay for both simulations in Figure 4.23 decays rapidly from 6.30 mg/L to 3.0 mg/L (moving from left to right on the Figure) within the first 20 to 30 km of

the system. The optimized chlorine decay model could predict the real chlorine decay within the system, as this same chlorine decay mechanism was observed for the temporal chlorine decay profiles that were validated by the experimental results, however the optimized chlorine decay model should be validated by the analytical values (Garcia-Avila et al., 2020, Goodarzi et al., 2020, Monteiro et al., 2017, Nono et al., 2018).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations of this study were based on the results of this study in relation to the achievement of the research study objectives.

5.1. CONCLUSIONS

This study successfully conducted laboratory experiments and developed computational and numerical models to investigate the decay and demand of chlorine accurate prediction of the chlorine residual necessary to meet minimum requirements and thereby ensuring the safety of the potable water supply from distribution systems.

The first-order chlorine decay models (including the PFOM model) are influenced by the reaction time of chlorine within the systems, both in terms of mathematical modeling and simulated chlorine residuals. This phenomenon is highlighted by the coefficient of determination, which ranges from 33.5% to 91.61% as the chlorine dose increases from 2.5 to 20 mg/L, respectively. Additionally, the bulk chlorine decay coefficient of the first-order model remains independent of chlorine decay dose, exhibiting an inverse linearity of 79.5% and 89.3% for slow and fast chlorine decay rates, respectively. However, the distribution of chlorine initial dose in slow and fast chlorine decay rates, as represented by the parameter (x), linearly decreases with a coefficient of determination of 92% as the chlorine dosage increases.

The second-order chlorine decay models (including the QCRS model) are dependent on the initial chlorine dose and chlorine residuals within the system, both in terms of simulated chlorine concentration profiles and mathematical models. This dependency is observed as the inverse chlorine residuals follow a linear trend with time, achieving a coefficient of determination ranging from 2.8% to 91.61% for chlorine dosages ranging from 2.5 to 20 mg/L, respectively. The bulk chlorine decay coefficient of the system linearly depends on the inverse chlorine dose, with a coefficient of determination of 98.2%, while the model parameter (R) is 96.6%.

The developed numerical models were well calibrated with both the experimental data and simulated temporal chlorine residuals. The significant chlorine consumption occurred within 15 minutes of reaction for all chlorine dosages, resulting in rapid chlorine decay within the 14 km network. Second-order chlorine decay models were best suited for situations with high chlorine demand, while first-order models are more suitable for lower total chlorine demand. The reaction of chlorine with both micro-organic and inorganic matter in the water is pH-dependent, but chlorine decay does not affect the water pH, which remained constant throughout the 4500 minutes of the experiment for all chlorine dosages. The modeling results enable the prediction of spatial and temporal changes in chlorine concentrations in the Vaalkop WTP network. At higher chlorine dosages above 10 mg/L, the formation of disinfection by-products (THMs) occurred within 250 minutes of reaction time. These THMs pose significant health risks and should be avoided by applying chlorine doses below 10 mg/L. The concept of breakpoint chlorination and the chlorine demand of the system exhibit a linear dependence on the initial chlorine dose and contribute to the development of an optimized chlorine decay model. This model estimates an initial chlorine dose of 6.30 mg/L, resulting in a

residual chlorine concentration of 0.60 mg/L without the formation of THMs, in accordance with the recommendations of the World Health Organization. The developed models could be utilized as an optimization technique to predict the actual chlorine residual within the system with 95% confidence.

5.2. RECOMMENDATIONS

Based on the findings/results of this study, several areas for future research have been identified:

- Development of a chlorine booster station in the Vaalkop water treatment plant distribution system: The main objective of this endeavor would be to ensure that there are sufficient chlorine residuals in accordance with the recommendations of the World Health Organization (WHO) and SANS 241 specifications.
- Utilization of in-situ experimental tests to determine decay coefficients: To achieve better results in simulating residual chlorine, it is advisable to use decay coefficients of the disinfectant that are obtained through experimental tests conducted within the specific distribution system under study. These coefficients should be determined with consideration for the conditions unique to the distribution network. Additionally, in modeling chlorine decay, the effect of pH values can be nullified to simplify the models.
- Calibration and validation of chlorine decay models: Model calibration and validation are crucial aspects of chlorine decay modeling, as they enhance the effectiveness and applicability of the model in real network systems. This should be prioritized to improve the accuracy and reliability of the chlorine decay models.

- Selection of appropriate modeling tools: When modeling traditional chlorine decay models, water quality models such as EPANET are suitable. However, for more complex or integrated models, the use of EPANET extensions like EPANET MSX (multispecies extension) and EPANET RTX (real-time extension) may be required. It is important to note that utilizing these extensions may necessitate knowledge of coding and can be time-consuming. Alternatively, solute transport models like COMSOL Multiphysics could be explored, as they provide the capability to model all chlorine decay models without the need for extensive coding knowledge.
- It is crucial to validate the predicted second-order chlorine decay model with experimental data. Implementing programs to maintain adequate levels of residual chlorine in the distribution network are preventive and protective measures that should be considered to prevent the spread of COVID-19 and other emerging pathogens.

By addressing these areas of research, further advancements can be made in understanding and modeling chlorine decay in water distribution systems, leading to improved water quality management and ensuring the provision of safe potable water to consumers.

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