# THE REACTION AND EFFECTS OF INORGANIC AND ORGANIC COMPOUNDS ON CHLORINE DEMAND IN WASTEWATER TREATMENT PLANT.


**by**

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Submitted in accordance with the requirements for the degree of

**MASTER OF SCIENCE DEGREE**

in the subject

**ENVIRONMENTAL MANAGEMENT**

at the

**UNIVERSITY OF SOUTH AFRICA**


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# Declaration

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I Sebati Florence declare that the research dissertation submitted herewith to the University of South Africa in partial fulfilment for the degree of Master of science in Environmental Management have not previously submitted by me for an academic degree at this or any other institution; I affirm that it is my own work from design through execution, and that all of the content included has been properly acknowledged.

Signature..... Date 19/11/2025

# Dedication

First and foremost, I dedicate this work to and thank the Lord Almighty God for providing me with the bravery and fortitude to keep going even when I felt like it would be hard. My utmost appreciation is next to my parents; my late "Dad Mathibedi William Sebati" and my mom Mampholodi Phostinah Sebati for inspiring me and my siblings to pursue further education and for demonstrating to us that one's upbringing does not define one's fate. My sincerest appreciation goes:

- To my siblings, "late brother Mmatshipi", Dr Ngwanamohuba, Mmatumela, Mmatladi and Mamphatlo Sebati for being my pillar of support; your words of wisdom and intercession have given me courage along this path;
- To my life partner Motsipiri Mojapelo and my Son Mathibedi Sebati whom I sacrificed time for to complete my studies;
- To my friends and extended family for their support during my academic career.

## Acknowledgement

I express my appreciation and thanks to the following individuals who I honor and respect. I'll be forever appreciative of the moral and professional assistance you provided me with during my study.

- My supervisor (Dr T.N Mhlongo) and Co- supervisors (Mr T. Mphaga & Mr R. Sekwele) for your unwavering efforts, wisdom, and direction in seeing my thesis through to completion;
- Andrew Wellam (Technician at SEWTREAT) for assistance with water sample collection;
- Kali Nkabinde (Lab technician at WATERLAB) for assisting with sample analysis;

I am grateful to the UNISA M&D bursary and National Research Fund (NRF) for their financial support in helping to finance my education.

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# Abstract

This study examines the efficacy of chlorine as a disinfectant used in most municipal wastewater treatment facilities. A large portion of the chlorine demand is eventually squandered because reactions that compete with the disinfection process produce chloramines and other byproducts that are unrelated to chlorine's main function of rendering water microorganisms inactive. The aim of the study is to investigate the reaction and effects of inorganic and organic compounds on chlorine demand in Wastewater Treatment Plant (WWTP). Influent and effluent samples were collected and analyzed at laboratory across four seasons; summer, autumn, winter & spring using standard methods. The physicochemical parameters assessed include pH, temperature, EC, ammonia, nitrate, COD, phosphate, chloride, chlorine residual and bacteriological indicators (*E-Coli*). Chlorine demand calculations were done for the plant. The results demonstrated a distinct seasonal fluctuation in the behavior of chlorine. While chlorine demand showed an inverse trend, rising in winter (0.47 mg/L) and falling in summer (0.13 mg/L), residual chlorine concentrations were highest in summer (0.37 mg/L) and lowest in winter (0.03 mg/L). This suggests that chlorine consumption rises during colder seasons due to higher pollutant loading. While effluent levels were high (4473–4907 MPN/100 mL), indicating insufficient disinfection, influent *E. coli* concentrations above 100,000 MPN/100 mL across all seasons. Correlation analysis showed that ammonia strongly correlated with COD (r = 0.811) and EC (r = 0.965), while temperature showed moderate positive correlations with SS and pH, and a strong negative correlation with nitrate. COD, nitrate, SS, phosphate, and chloride all showed positive correlations with chlorine demand, suggesting that higher concentrations of these parameters increase chlorine demand. Temperature, ammonia, pH, and EC all showed negative relationships, indicating that these variables were within ranges that did not considerably raise chlorine consumption. Regression analysis between dependent and independent variable indicates a perfect correlation R (1.000) between the observed and predicted values for chlorine demand. Although some parameters like pH, temperature, EC, and residual chlorine were within

the acceptable limits, others including nitrate, ammonia, phosphate, COD, and E. coli did not conform to the recommended limits of WHO, 2007. Elevated levels of organic and inorganic contaminants were found to greatly increase chlorine demand, decrease the effectiveness of disinfection and promoting the formation of harmful disinfection byproducts. The study concludes that insufficient removal of organic debris and nutrients reduces the efficiency of chlorine, endangering human health and the environment. Improved pretreatment and nutrient removal techniques are recommended to improve disinfection efficiency, reduce chemical costs, and minimize ecological impacts like toxicity and eutrophication in receiving water bodies.

## Key Words

Wastewater Treatment

Physicochemical Parameters

Microbial Parameters Disinfection

Chlorine Demand

Disinfection by-products

# List of acronyms

| | |
|---|---|
| BOD | Biological Oxygen Demand |
| COD | Chemical Oxygen Demand |
| EC | Electrical conductivity |
| $NH_3$ | Ammonia |
| $NO_3$ | Nitrate |
| pH | Potential Hydrogen |
| TSS | Total suspended Solid |
| WWTP | Waste Water Treatment Plant |
| SWTR | Surface Water Treatment Rule |
| ERWAT | Ekurhuleni Water Care Company |
| DWS | Department of Water and Sanitation |
| DWA | Department of Water Affairs |
| $PO_4^{(3-)}$ | Phosphate |

| | |
|---|---|
| $NaOCl$ | Sodium Hypochloride |
| $THMs$ | Trihalomethanes |
| $HOBr$ | Hypobromous acid |
| $OBr$ | Hypobromite |
| $TN$ | Total nitrogen |
| $N_2$ | Nitrogen gas |
| $Fe^{3+}$ | Iron(III) ion |
| $Br_2$ | Bromine |
| $Cl^-$ | Chloride ion |
| $DOC$ | Dissolved Organic Carbon |

# CHAPTER 1

# Introduction

## 1.1. Background

Chlorine is a disinfectant that is widely used globally, because of its efficiency and affordability (Madzivhandila and Chirwa, 2017; Zhang *et al.,* 2020). There are numerous methods that can be used for disinfection, and this includes physical methods like filtration, ultraviolet radiation and chemical methods such as chlorine gas and sodium hypochlorite solution ($NaOCl^-$). Chlorine is used in most wastewater treatment plants globally and in South African municipal water agencies for disinfection before releasing the trated effluent back into the environment or waterbodies (Silva *et al.*, 2010; Jachimowski, 2018). Water disinfection implies inactivation and killing harmful microorganisms, is used to meet *Escherichia coli* and fecal standard specified by South African general and special limits for wastewater effluent (DWS, 2017).

Chlorine is capable of deactivating pathogens on contact with wastewater such as bacteria, viruses, and protozoa in water (Silva *et al.*, 2010). Chlorine reduces odor and bitterness in water, kills harmful bacteria, viruses, and protozoa, and stops algae and mold growth in the water supply reservoirs. However, chlorine oxidizes organic materials and is known to produce hazardous and mutagenic by-products including trihalomethanes (THMs) which are toxic towards aquatic life and humans (Jachimowski, 2018; Tak and Vellanki, 2018). It is confirmed that chlorine disinfectant by-products are a cancer-causing agent and blamed for reproductive or developmental effects (Tsitsifli and Kanakoudis, 2018; Joo and Choi, 2021). Chlorine reacts with both suspended and dissolved solids in water leading to its uptake through oxidation of organic and inorganic matter thereby decreasing its concentration and therefore its efficiency (Roth and Cornwell, 2018).

Chlorine produces compounds that create high chlorine demand. When added to wastewater, chlorine also reacts with organic and inorganic compounds as it is reactive chemical (Madzivhandila and Chirwa, 2017). In the process of disinfection

nitrate react with chlorine to form chloronitromethanes and can generate nitrogenous disinfection by-products (Lin *et al.*, 2021). The compounds include reduced metals, sulfides, bromine ions, organic and inorganic nitrogenous compounds (Zimoch, 2011; Jachimowski, 2018). Chlorine reacts with ammonia and bromine to form chloramines and hypobromous acid respectively; both of which are deleterious to human aquatic species. These factors increase the chlorine demand and increasing the chlorine dosage as a counter measure leads to accumulation of residual chlorine in wastewater (Roth and Cornwell, 2018; Li *et al.,* 2020). Chlorine demand is the difference between the quantity of added chlorine to water and the amount of residual chlorine that is left over after a specific contact time. It is the amount of chlorine that remains after adding residual chlorine to water but is not usable for disinfection (Netshidaulu, 2015).

The demand of chlorine changes with dosage, duration, temperature, pH and water impurity levels (Jachimowski, 2018; Wu and Dorea, 2020). Free chlorine becomes available once compounds demand is satisfied (Kowal and Świderska-Bróż, 2009). Breakpoint chlorination, which is a waste since more chlorine is overwhelmed than is required for disinfection, occurs when the chlorine demand is satisfied by substances other than disinfecting bacteria. The cost of chlorine required for disinfection at treatment plants rises because of breakpoint chlorination (Netshidaulu, 2015; Karthik et al., 2020). However, as noted by Frumina and Gildeeva (2014), excessive loading of nitrogen and phosphorus from point source and non-point source pollution can occur in water bodies when chlorine levels are low to prevent negative health effects. This results in eutrophication conditions and the depletion of aquatic species.

Numerous studies indicate that while applying a disinfectant, it is important to take into account various aspects, including contact time, disinfectant concentration, organism type, age, and number, effluent elements, temperature, chlorine demand, and mixing (Doederer *et al.*, 2014; Netshidaulu, 2015; Abokifa *et al.*, 2016; Tsitsifli and Kanakoudis, 2018; Paleologos *et al*., 2021; Giacobbo *et al.*, 2021). The most important factor in the disinfection process is the amount of time that the disinfectant and wastewater are in contact. In general, disinfection is more effective during longer contact times for any given concentration (Kong *et al.*, 2021; Jalali Milani, and Nabi Bidhendi, 2022). when the disinfectant concentration is increased in milligrams per

liter, the amount of time needed to kill specific germs decreases (Netshidaulu, 2015; Kong *et al.*, 2021).

It is recommended that the quantity of chlorine in drinking water must not exceed 5 mg/L, as it is normally needed for little more than 0.4 mg/L to kill germs (WHO, 2017). Chlorine concentrations supplied to effluent are often high because of the high demand for chlorine in wastewater treatment facilities (Roth and Cornwell, 2018). The concentration of organisms can occasionally be a significant factor in the wastewater treatment process; the greater the counts/100 mL of organisms, the higher the disinfection concentration (Netshidaulu, 2015). Disinfecting young bacteria is easier than disinfecting the fully grown bacteria. As these bacteria age, their cell walls get covered in a polysaccharide shell, which increases their resistance to disinfection (Okpara *et al.,* 2011).

Wastewater treatment utilities test the presence of other microorganisms using an indicator organism such *Escherichia coli*. Absence of *Escherichia coli* does not necessarily mean that water is safe since other disease-causing agents such as enteroviruses and protozoa are more resistant to chlorine (Mhlongo *et al.,* 2020). Not only does the discharged water with the chlorine have compounds that increase the chlorine demand, but also the by-products escape to nearby streams. The by-products are not biodegradable; therefore, they end up accumulating in tissues of aquatic species such as fish, leading to these by-products affecting organisms that are at higher trophic levels including humans.

In South Africa, there has been an escalating growth of informal settlements around rivers (Chezhien *et al.,* 2010; Jooste *et al.*, 2015; Sibanda *et al.*, 2015). When sources of water such as rivers are contaminated by chlorine disinfectants by-products, they can negatively affect the community as they may tend to use the water as sources for drinking purposes and other activities such as fishing, leading to sicknesses. The current study aims to investigate the factors that influence high chlorine demand in wastewater treatment plants (WWTP).

## 1.2. Problem statement

Chlorine has contributed to the reduction of morbidity emanating from waterborne illnesses (Haushofer *et al.,* 2021). However, the addition of chlorine in wastewater has been shown to increase the reaction of chlorine with organic and inorganic compounds that have been linked to harmful effects on public health (Roth and Cornwell, 2018). Mutagenic and dangerous by-products such as THMs are harmful to human and aquatic species (Jachimowski, 2018). THMs such as chloroform, dibromochloromethane (DBCM), bromodichloromethane (BDCM), bromoform and haloacetic acids (HAAs) are responsible for mutagenic and carcinogenic effects on living organisms. It has been demonstrated that THMs are potentially genotoxic and mutagenic towards humans and have been associated with bladder, colorectal and brain cancers in addition to spontaneous abortions; all of which are worsened by the prevalent long-term exposure (Chowdhury, 2013; Dehghani *et al.,* 2016; Azizl *et al.*, 2017). THMs are assimilated into the human body through multiple channels such as ingestion, inhalation and dermal contact and as well as drinking water consumption. Concerns over THMs exposure are exacerbated by the high concentrations of THMs that have been found in drinking water (Sadeghi, 2019). According to WHO (2011) total THMs concentration should not exceed 100 µg/L. Despite these standards, effluents are often laden with THMs and other persistent and non-biodegradable pollutants leading to their accumulation in the aquatic and associated environments (Yadav *et al.,* 2009). This alters the natural balance drastically in the environmental water quality and leads to raising the amount of public health concerns (Schwarzenbach *et al.,* 2010; Vargas *et al,* 2014).

In the process of disinfection, chlorine ($Cl_2$) reacts with water to form hypochlorous acid (HClO) and in the presence of bromine, hypobromous acid (HBrO) is formed as well (Yang *et al*., 2014). Tak and Vellanki. (2018) found that HClO and HBrO also react with naturally occurring organic matter (NOM) to create a wide variety of water disinfection by-products, including chloroform - $CHCl_3$, bromodichloromethane (BDCM) - $CHCl_2Br$, Dibromochloromethane (DBCM) - CHClBr and bromoform - $CHBr_3$ and these increase high chlorine demand in water (Kuzniewski, 2021; Kong *et al.,* 2021). Organic matter, mainly humic compounds, play a major part in the formation of

undesirable organic by-products following the disinfection of wastewater. Most disinfection by-products have unfavorable carcinogenic or mutagenic effects on human health (Richardson *et al*, 2007; Kohpaei and Sathasivan, 2011; WHO, 2011) These factors drive the operational costs of chlorine disinfection and also lead to reduced disinfection efficiency of the final effluent. As a remedy, it is important to understand the chemical reactions that occur concurrently during chlorination. Kong *et al., (*2021) discovered that if there is low organic matter in the effluent, the reaction of disinfection will be faster. They further reasoned that a chlorine dosage lower than 0.4 mg/L could be enough for disinfection. In wastewater, chlorine oxidizes particular organic matter constituents to create THMs which are more hazardous (Silva *et al*, 2010; WHO, 2017; Roth and Cornwell, 2018).

According to Liu *et al*., (2019) ammonia, which is a compound of hydrogen and nitrogen ($NH_3$), is colorless gas derived from wastewater effluent and anaerobic digestion liquid from wastewater treatment plants. It is also naturally generated from the decomposition of organic matter such as that derived from plants and animals. Ammonia is used in industries and exists naturally in human as well as the environment. (Liu *et al.*, 2019). Ammonia reacts with chlorine to form chloramines which hamper the disinfection process, leading to the accumulation of residual chlorine in effluent recipient surface waters such as rivers and an increased toxicity thereof (Roth and Cornwell, 2018; Liu *et al.*, 2019). It negatively affects aquatic species and may lead to eutrophication as well as species extinction.

A study conducted by Collivignarelli, (2017) in Italy mentioned that wastewater treatment should ensure health security and microbial quality. According to wastewater regulations, *Escherichia coli* levels cannot be higher than 5000 CFU per 100 mL, and the active chlorine content should be less than 0.2 mg/L with no acute toxicity. The general limit, which is 1000 CFU per 100 mL, is more stringent in South Africa (DWAF, 2013). According to Vargas *et al*., (2021) during the period when chlorine and water are in contact, the rate at which inorganic compounds react with chlorine is faster than that of organic molecules. Consequently, a larger dosage of chlorine is needed, which raises the chlorine demand.

## 1.3. Justification

The right of humans' access to a sufficient supply of safe drinking water is a universal regardless of their development stage, social and economic conditions (Water Services Act, 1997; WHO, 2011). The Department of Water and Sanitation (DWS) requires 0.1 mg/L free chlorine as a general limit of discharge of wastewater effluent to the environment and non-detection of residual chlorine (WHO, 2017). According to South African National Water Act No.36 of 1998 (NWA), local authorities are allowed to discharge only treated effluent to water bodies or the environment as it is obligatory to return treated wastewater to the source. This Act specified and published the required standards to be met when treated effluent is discharged to the environment to solve water quality problems such as eutrophication and desalinization (DWS, 2017). The study aims to analyze the occurrence of organic and inorganic compounds via in-situ analysis and further profile *Escherichia coli* occurrence in surface waters to ensure that they meet the required standards for the release of effluent to the environment.

The DWA brought up concerns about pollution from deteriorating municipal wastewater treatment plants which pose risks to water quality (DWA, 2013a). Many harmful substances that can harm receiving streams are thought to be present in wastewater, which could endanger human health and cause ecological imbalance. It is widely accepted that wastewater must be treated before discharged into waterways (Edokpayi *et al.,* 2017). The green-drop program was created to safeguard human health and receiving watersheds from the dangers of releasing low-quality wastewater. Accordingly, the green-drop standards seek to recognize South African water utility bodies that adhere to wastewater legislation and other best practices. This strategy was developed and put into practice in South Africa, and it is recognized globally as being distinct in the field of water regulation. (DWA, 2011, 2015).

The entire wastewater treatment process is the focus of this incentive-based strategy. Through the recognition of excellence in the field, it is thought to be a significant motivator for the improvement and assistance of the nation's inadequate wastewater management practices (ERWAT, 2018). Section 21 (f) of (NWA) permits wastewater to be discharged into a water resource only if the individual or organization is license.

Most wastewater treatment facilities do not adhere to the regulations needed to release their effluent into the environment. According to the findings by Samie *et al.,* (2009) on the effectiveness of sewage treatment facilities in the South African province of Mpumalanga, only two out of fourteen wastewater treatment facilities had zero levels of fecal indicator species. In addition, they pointed out that there aren't many wastewater treatment facilities in the area in relation to the population they serve. During their six-month monitoring period, Edokpayi *et al.,* (2018) observed that Siloam Waste Stabilization Ponds and the Thohoyandou wastewater treatment plant in South Africa's Vhembe District were releasing effluents high in fecal indicator species at levels beyond the advised limits. There is a noticeable level of dysfunction in the way municipal wastewater treatment facilities are managed. The most recent Green Drop report serves as an example of this, rating nearly 50% of 824 facilities of municipal wastewater treatment works as "critical" or "poor." As a result, water courses are heavily contaminated with nutrients and pathogens from untreated or insufficiently treated sewage effluent from these facilities (DWS, 2017).

It is critical to monitor organic and inorganic compounds in treatment works as they create chlorine demand when reacting with chlorine. Satisfying chlorine demand is cost apprehensive because more chlorine is consumed for disinfection than is required. The consequences are that the cost of chlorine increases at the wastewater treatment process for the required disinfection (Okpara *et al.,* 2011; Netshidaulu, 2015). There is poor disinfection observed at certain plants despite sufficient chlorine dosages. This is due to the lack of upstream modification to process technology and other plant process not being optimized (DWA, 2011, 2012).

The United Nations Sustainable Development Goals (SDG) 3.3 and 3.9 is aimed at ending water borne diseases, reducing death and illness number from water contamination by 2030 (Leal-Filho *et al.,* 2019; Scanlon, 2022). Despite the awareness on the SDGS, 44% of municipal wastewater treatment works still discharge untreated effluent to water bodies and the environment (Massyn *et al.*, 2020). In this regard, it may reduce the quality of drinking water as well as contaminating underground water that led to the Water Institute of South Africa (WISA) (2020) saving the mothball of Blue Drop and Green Drop certification programme since 2014 (Massyn *et al.*, 2020).

The aim of the study is to investigate the influence of organic and inorganic compounds on chlorine demand in wastewater treatment plant. Numerous studies have been conducted on the influence of high chlorine demand in water (; Gile, 2016; Netshidaulu, 2015 and Collivignarelli *et al.*, 2017). The majority of research was done outside South Africa in places such as Arkansas (USA), Italy, Tehran (Iran) and Brazil, and used full scale analysis (Gile, 2016; Collivignarelli *et al.*, 2017; Vargas *et al.*, 2021). There is no study that was conducted in the selected study area, for that reason there is insufficient information concerning chlorine demand that will assist in chlorine optimization and budget control associated with disinfection. This study will focus on inorganic, organic and physicochemical parameters such as pH, electrical conductivity (EC), ammonia, temperature, nitrate, chloride and phosphate, total suspended solids (TSS), chemical oxygen demand (COD), *Escherichia coli*, contact time and residual chlorine. Parameters were selected because multidisciplinary research conducted outside South Africa has shown that they are problematic (Gile, 2016; Collivignarelli *et al.*, 2017).

Chlorine is a potent oxidant that is frequently used in oxidation and disinfection procedures like pre-treatment oxidation and primary & secondary disinfection (USEPA, 2015; Tak and Vellanki, 2018). The amount of added chlorine in wastewater is related to the source of water, the chlorine amount that is required for chemical reactions leaves the available free chlorine for proceeding disinfection. While chlorine begin with the disinfection in water, most studies found that chlorine led to formation of disinfection by-products (DBP) when reacting with organic and inorganic contaminants (Kohpaei and Sathasivan, 2011; Roth and Cornwell, 2018; Kong *et a*l., 2021).

In United State (US), US Environmental Protection Agency (USEPA) set maximum contaminant levels of 0.080 mg/L for trihalomethanes and 0.060 mg/L for haloacetic acids, two major classes of disinfection by-products unique to treatment chlorine (USEPA, 2006). The surface water treatment rule (SWTR), which mandates that the utilities for drinking water maintain a quantifiable disinfectant residual across the distribution system, has also developed requirements (USEPA, 2004).

The source of water can affect the amount of chlorine demand needed and therefore

it is critical to comprehend the connections between sources of water and chlorine demand (Tak and Vellanki, 2018). This information can be used to optimize the plant for adequate pollutant removal, lowering the dosage of chlorine and meeting demand without leaving residues over environmental standards. The water source has been demonstrated to impact chlorine demand because chlorine reacts with variety of substances including ammonia ($NH_3$), nitrate ($NO_3$), organic and inorganic matters, iron (Fe), manganese (Mn) and many more to form trihalomethanes (THMs), haloacetic acids (HAA) and chloramines which are dangerous to the environment and human health as well (Collivignarelli *et al.*, 2017).

## 1.4. Research aims and objectives.

### 1.4.1. Main Objective (aim)

To investigate the influence of inorganic and organic compounds on chlorine demand in Wastewater Treatment Works (WWT).

### 1.4.2. Secondary objectives

- To collect wastewater samples on the final effluent to conduct in situ analysis of initial physico-chemical tests such as pH and temperature that affect chlorine dosing.

- To collect wastewater samples on final effluent for analysis of microbial parameters including *Escherichia coli.*

- To collect wastewater samples on selected stages of wastewater treatment for analysis of inorganic compounds such as ammonia ($NH_3$), phosphate

- ($PO_4$) and nitrate ($NO_3$) and organic compounds such as TSS, COD and chloride.

- To determine the actual chlorine demand and compare with the design chlorine demand in wastewater disinfection system.

- To monitor chlorine residual at final effluent discharge point to determine the distribution of chlorine that causes toxicity to the river.

- To determine the statistical correlation between the presence of inorganic compound and organic compounds with chlorine dosing and residual chlorine and link to chlorine demand.

## 1.5. Research questions

### 1.5.1. Main research question

Do inorganic and organic compounds have influence on chlorine demand?

### 1.5.2. Subsidiary questions

- What test can be done to evaluate the influence of inorganic and organic compounds on chlorine demand?

- How are indicator variables including temperature, pH, organic and inorganic compounds influenced by chlorine dosage?

- What is the actual chlorine demand compared to the design chlorine demand for in wastewater disinfection systems?

- What is the concentration of free chlorine residual that causes toxicity in receiving rivers?

- What is the statistical correlation between the presence of inorganic compounds and organic compounds with chlorine dosing and residual chlorine and link to chlorine demand?

# CHAPTER 2

# Literature review

## 2.1. Introduction

Natural organic matter (NOM) is a combination that is consisted of different heterogeneous chemical portions having varying polarity charges and chemical makeup as well as molecular weights. The presence of NOM in water can lead to the formation of Disinfection By- Products (DBPs) and other water quality issues of concern (Nebbioso and Piccolo, 2013). NOM comes from microbes, plants and mammals. DBPs formation is a result of NOM interactions with factors such as TSS, COD, $Cl^-$ and $Br_2$. DBPs are mainly responsible for issues of water quality attributes including color, taste and odor (Sillanpää, 2014). The origin of NOM is described as autochtonous and allochtonous which means that the NOM originates from the water source or it is sourced from elsewhere other than the water source (Berggren *et al.*, 2015). DBPs is also formed in the interaction of inorganic compounds that include a combination of metals, salts, particles, and mineral complexes that have no presence of carbon. These pollutants include both natural and human-made elements that can contaminate water such as $NH_3$, $PO_4$ and $NO_3$ (Kohpaei and Sathasivan, 2011; Merz, 2013). They are sourced from industrial pollution, illegal dumping, uncontrolled spillages into storm water and domestic wastewater resulting in them eventually getting into wastewater treatment works (WWTWs) and increasing the chlorine demand (Singh *et al.*, 2018).

Chlorine is a disinfectant that is often as sodium hypochloride (NaOCl) or gaseous chlorine (Simya*,* 2019). When it reacts with organic and inorganic compounds, it leads to the formation of by-products like trihalomethanes (THMs) and haloacetic acids (HAAs) that are harmful to human and aquatic life (Silva *et al.,* 2010). It was confirmed that chlorine disinfection by-products are substances that causes cancer and have been blamed for deleterious reproductive effects (Tsitsifli and Kanakoudis, 2018; Singh *et al.*, 2018). Numerous epidemiological investigations have confirmed that THMs cause severe health effects (Wang *et al.,* 2013; Villanueva *et al.,* 2015). NOM's

interaction with chlorine depends on the chemical characteristics of NOM. For example, THMs are generally formed via the reaction between NOM and chlorine and can be produced by wastewater treatment facilities (Yang *et al.*, 2014).

Chlorine interacts with both organic and inorganic substances to create high chlorine demand. Inorganics substances like iodide, bromide, nitrate and ammonia cause the formation of nitrogenous (N-DBPs), brominated (Br-DBPs), and iodinated (I DBPs) compounds that increase the chlorine demand in water (Dong *et al.*, 2019). These DBPs are mostly more toxic and carcinogenic depending on the chemistry of the compounds (Huang *et al.,* 2019). Bromide is typically found in natural water and can enter wastewater as a result of industrial activities. Chlorine reacts with bromine to form hypobromous acid/hypobromite ($HOBr/OBr^-$). HOBr acid is a weak acid but when it reacts with organic matter it forms highly toxic BrDBPs. Once Br-DBPs are created they are difficult to remove leading to their accumulation in aqueous environments (Li *et al.*, 2020).

Inorganic compounds react more quickly with chlorine than organic compounds depending on their chemistry and the contact time and this increases the dosage of chlorine leading to high chlorine demand in water (Vargas *et al.*, 2021). According to Gile, 2016, chlorine dose and mean chlorine demand has been observed to increase with NOM, $Fe^{3+}$, $Mn^{2+/3+/7+}$, total nitrogen (TN), temperature, turbidity, and TSS and decreased with the increase of conductivity, pH, and alkalinity. High levels of COD in wastewater reduce the reaction of chlorine with *Escherichia coli* and faecal coliforms. According to a study by Li *et al.,* (2021), as the COD level increased in the range 600–800 mg/L, the chlorine inactivation coefficient for *E. coli* O157:H7 dropped by almost 73%. This result emphasizes how COD levels and chlorine disinfection effectiveness are inversely correlated.

A high ammonia concentration naturally causes free ammonia to be present under alkaline conditions. Liu *et al.*, 2019; Kong *et al.,* 2021 discovered that temperature, pH, organic matter and turbidity have an influence on disinfection efficiency. Chlorine disinfection efficiency is measured by the CT factor-which is the amount of chlorine (C) multiplied by the contact time (T). A temperature of 10 °C increases the CT value

required to remove certain virus and in general low pH promotes disinfection while high pH impedes disinfection.

Most of the disinfection by-products function as possible mutagens and carcinogens for humans, that have been not only been associated with cancers such as rectal and colon cancers but also reproductive and developmental problems (Silva *et al.*, 2010; Joo and Choi, 2021). In addition, DBPs can be transported to groundwater and contaminate it over time. They also seep into the soil, to react with organic and inorganic materials; in the process reaching sewer lines and eventually wastewater treatment works where they undergo partial treatment. When chlorine compounds reach sewer systems many DBPs may be created based on the presence and concentration of NOM, inorganics and anthropogenic pollutants (Parveen *et al.*, 2022).

On the discharge of wastewater to the environment, most chlorine-based disinfectants (CBDs) emit free chlorine which combines with organic materials to create DBPs. Inorganic constituents and physicochemical parameters like pH, temperature and disinfection by-products may form THMs, HAAs, haloacetonitriles (HANs), haloketones (HKs), and trihalophenols (THPs) based on the type of the organic matter (Li *et al*., 2021; Wang *et al*., 2021).

## 2.2. Review of past studies

### 2.2.1. The influence of inorganic and organic compounds on water quality

Water quality influences chlorine demand because chlorine interacts with a variety of substances including ammonia ($NH_3$), nitrate ($NO_3$), NOM, $Fe^{3+}$, $Mn^{2+/3+/7+}$, TSS, COD and bromine to form THMs, hypobromous acid, chloronitromethane (Abdullah, 2009; Lin *et a*l., 2021). In addition to the water treatment practices, raw water components also influence chlorine demand. Chlorine interacts with the organic and inorganic components in water to form DBPs. NOM has been shown to be strongly reactive with chlorine. Reactions between NOM and chlorine occur mainly through process of oxidation and substitution in which chlorine replaces a functional group in NOM compounds (Gile, 2016). NOM is a combination of humic and non-humic materials, it is frequently expressed using metrics such as total organic carbon (TOC), ultraviolet

disinfection and dissolved organic carbon (DOC). The majority of water's chlorine requirement depends on the concentrations of NOM and these concentrations have been shown to fluctuate with seasons (Chaulk and Sheppard, 2011). A high concentration of NOM can lead to high chlorine demand which results in elevated water treatment costs as well as higher possibility DBPs formation.

While studies have also observed that NOM makes a significant contribution towards an increased chlorine demand, chlorine depletion due to its reactions with inorganic compounds and microorganisms cannot be ignored (Doederer *et al.*, 2014; Abokifa *et al.*, 2016). Chlorine reduces dissolved metallic ions such as Fe (ll) and Mn (ll) to form insoluble Fe (lll) and Mn (lll;IV). The metallic ions $Fe^{3+}$ and $Mn^{2+}$ are typically discovered in soluble form at lower pH levels and in anoxic environments. These elements tend to occur soluble form at higher concentrations during the summer months (Brezonik and Arnold, 2011). Microorganisms in water oxidize ammonium ($NH_4^+$) to form nitrate ($NO_3^-$) through the nitrification process and reduce the $NO_3^-$ to nitrogen gas ($N_2$) through denitrification process. Chlorine also oxidizes ammonia, and as the ammonia concentration increases, breakpoint chlorination is reached (Karthik *et al.*, 2020). Additionally, this oxidation process comprises intermediatory products like various kind of chloramines and the distribution of the reaction products depend on pH. *Escherichia coli* as an indicator organism also has influence on the water quality. Netshidaulu, (2015) revealed that the inactivation of *Escherichia coli* carried out in a full-scale chlorine system is less effective than the expected one under laboratory conditions. However, substantial inactivation can be attained when mixing is performed at the chlorination point. It was discovered that when a particular ideal mixing schedule is chosen and implemented at the chlorination point, an effective inactivation of *Escherichia coli* in the water is attained. However, high levels of COD in wastewater reduces the reaction of chlorine with *Escherichia coli* and fecal coliform (Roth and Cornwell, 2018).

### 2.2.2. The impact of inorganic and organic compounds on chlorine demand

Inorganic and organic compounds have been discovered to have a great influence on chlorine demand. However, this also depends on the type of disinfectant and contact

time. According to Netshidaulu, (2015) the more the contact time, the more COD is reduced. High level of COD in wastewater reduces the reaction of chlorine with *Escherichia coli* and fecal coliform (Roth and Cornwell, 2018) and this increases the level of chlorine demand. Chemical's impact on chlorine demand depends on concentration, chemical structure and rate of reaction (Teng, 2018). Organic compounds provide abundant substances that support the growth of microbes and have to be removed to meet standards for water regulations. These compounds generate high chlorine demand resulting in quick reduction in free chlorine.

According to Parveen *et al.,* (2022), depending on the amount of organic, inorganic, and anthropogenic contaminants present when chemicals containing chlorine enter the sewer system, these compounds get exposed to wastewater and can produce a variety of disinfection byproducts. Hospital effluent can be chlorinated to produce dangerous drug-derived disinfection byproducts, many of which are human cancer-causing and some of which are cytotoxic, genotoxic, and mutagenic. DBPs could be detrimental on the presence of microbes and plankton in the ecosystems as well as being hazardous to the plants and animals in the receiving water body. Utilization of chlorine should rise in order to reach the ideal chlorine dose when there is a high organic load in the treatment plant (Abdo *et al.*, 2022).

Studies conducted by Friedler *et al.,* (2021) on treated domestic greywater from the eleven single-family full-scale recirculating vertical flow constructed wetland have revealed that poor quality of water can reduce the effectiveness of chlorine and UV disinfection. In particular, the existence of organic matter and particle matter in the water may have a negative impact on the efficacy of chlorine and UV radiation treatments. An increase in the chlorine demand is a sign that chlorination is having a negative effect because chlorine oxidizes suspended and dissolved organic materials. As a result, disinfection loses some of its effectiveness. Microorganisms have a reduced chance of coming into contact with chlorine when they stick to water-borne particles than bacteria that aren't related.

Another technique for detecting organic contamination in water is the measurement of COD, which is measured in mg/L. It is the concentration of dissolved oxygen required

to oxidize organic molecules in water chemically. In order to measure the COD in water, the water sample must first react with a strong oxidizing agent, which oxidizes any organic materials present. It is well-known and rapid substitute test for BOD for figuring out how much organic matter is in wastewater samples is COD. A surface water supply's BOD and COD levels are recognized as crucial environmental health indicators. However, they are rarely employed in the treatment of common water supplies (Patil *et al.,* 2012). To assess the level of home and industrial sewage contamination, this COD test is frequently employed (Baharvand and Daneshvar, 2019).

The level of organic material water contamination is determined by COD levels, the traditional method for detecting COD necessitates chemical sample preparation and pre-treatment. These traditional methods require a lot of time and effort (Alan, 2015). The quantity of contamination in the water sample increases as the COD increases. However, one crucial quality control factor for an effluent in a wastewater treatment facility is COD (Wu *et al.,* 2011). High COD and SS are related to high organic content in wastewater

A strong demand for chlorine from organic components causes free chlorine to be depleted quickly (Teng *et al.,* 2018). Concentrated sodium hypochloride can be added to restore free chlorine, but doing so repeatedly in water with a lot of organic matter can make it ineffective and create harmful chlorine byproducts. Organic substances may significantly reduce the efficacy of chlorine disinfection by stabilizing bacterial cell walls. Organic waste can impede the disinfection process and create health risks by causing the production of unintended disinfection byproducts, such as known or suspected carcinogens (Onga *et al.,* 2019).

To properly dispose of the effluent in a recipient aquifer, wastewater treatment plants (WWTPs) typically concentrate on the removal of nutrients and suspended particulates. However, as germs are not eliminated after treatment, WWTPs may be a source of the dispersal of microorganisms in the environment (Guadagnini *et al.,* 2013; Numberger *et al.,* 2019). The suspended particulate matter, which influences the optical characteristics of water bodies and may be detected from remote sensors, is

one of water's main elements. It is crucial to understand their chemical makeup because whether they are mostly made of organic or inorganic substances will affect the ecological function they serve in water bodies (Alvado *et al.,* 2021).

### 2.2.3. Wastewater treatment process

Domestic, commercial, industrial, and storm water are all types of wastewaters that need to be treated before being released into the environment to reduce risks to the environment and human health (Edokpayi *et al.,* 2017). A wastewater treatment plant's goal is to securely dispose of wastewater produced during water consumption by eliminating or decreasing contaminants while minimizing any adverse impacts on the environment and human health (Edokpayi *et al.,* 2017; Agoro *et al.*, 2018). According to Iloms *et al.,* (2020), numerous studies demonstrate that the majority of municipal WWTPs in South Africa cannot sufficiently treat their wastewater to the required levels, leading to the direct release of effluents that contaminate recipient waters. As evidenced by instances of non-adherence to national water resources legislation, regulations, and norms and standards designed to safeguard the SA's water resources; inadequate and poor WWTPs are regarded as the main reason for contamination of water in SA. (Ntombela *et al.,* 2016a)

Owing to the technologies in use being unable to manage the rising pollutant loads, and due to the degree of development in different towns, population expansion is one of the key drivers of wastewater pollution (Naidoo and Olaniran, 2014). Different techniques are used by WWTPs to reduce or remove hazardous pollutants from wastewater. The three stages of the therapy process—primary, secondary, and tertiary treatment—each having their own unique biological, physical, and chemical processes—are used to classify the water treatment process (Naidoo and Olaniran, 2014). **Figure2.1** breaks down these treatment stages into the subsidiary processes for each stage.

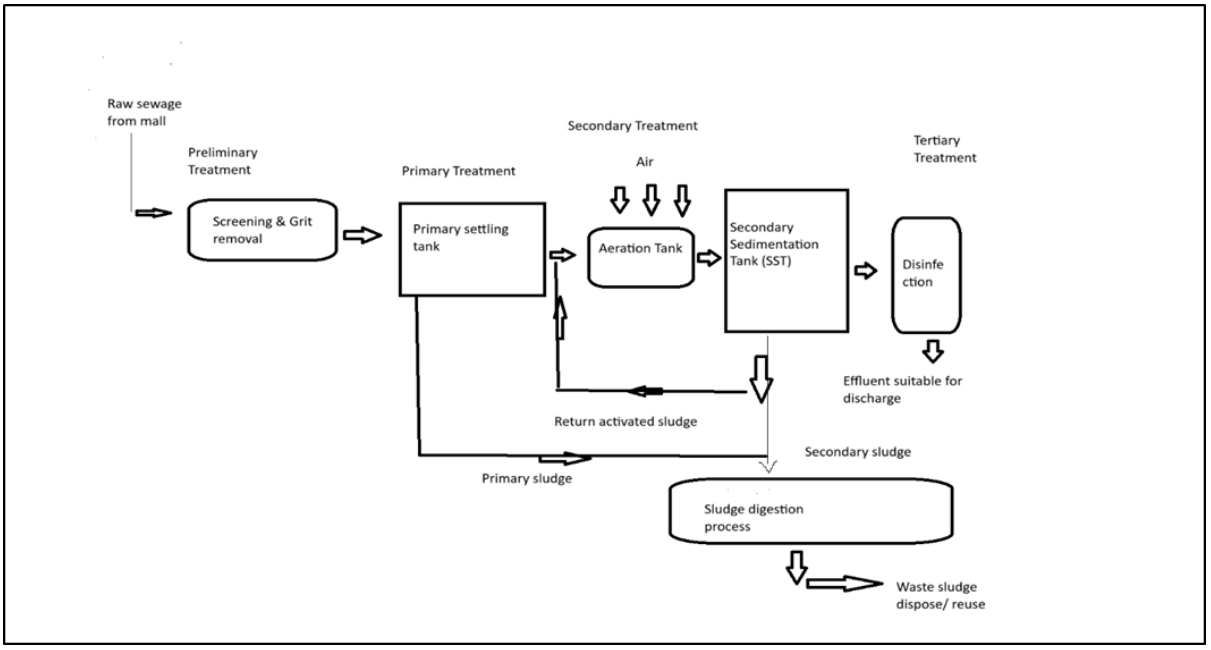


*Figure 2.1: Different stages of WWTP (Paint).*

### *I. Primary treatment*

The main treatment step primarily consists of the physical removal of any suspended materials present in the wastewater, such as oils, fats, and grits. At this point, the wastewater still contains suspended solids that were eliminated during the separation of the solid and liquid phases, as well as dissolved organic and inorganic chemicals. Additionally, this procedure enables the sludge to be treated anaerobically because solids having a higher specific gravity than the liquid settles near the bottom of the settling tank and those with a lower specific gravity move upwards (Naaidoo and Olaniran, 2014)

- ❖ Screening

The wastewater treatment process starts from screening, where large objects are trapped. Manual cleaning is done on the screen. The screen must be cleaned every day because obstructions could result in odors and/or overflow situations. Lime is added to reduce odor and nuisance insects. Screeners are taken by a contractor for disposal and screened effluent flows to the buffer tanks for further treatment (Metcalf and Eddy, 2014)

- Buffer tank

Wastewater in the buffer tanks moves slowly so that it can settle for several hours, thus reducing the number of solids in the wastewater and letting the heavier material settle to the bottom of the tank to create primary sludge. Desludging of the tank takes place to remove the accumulated sludge and settled effluent flows to the anaerobic reactor where the secondary treatment process starts (Metcalf and Eddy, 2014)

### *II. Secondary treatment*

The biological methods used in secondary treatment are primarily responsible for removing the remaining organic matter in the wastewater. The liquid that emerges from the primary settling tanks is subsequently oxygenated. A number of secondary treatment procedures exist, and they include bio-filters, the activated sludge process, various types of ponds, and artificial wetlands (Naaidoo and Olaniran, 2014; Hansen, 2015). The most popular method is called activated sludge, and it involves pumping buffer tank effluent into an anaerobic reactor, which is populated with microorganisms that thrive in low-oxygen settings (SEWTREAT, 2023). The reactor allows digestion of sewage and the separation of solids while COD is converted to carbon dioxide and methane.

- Anaerobic reactor

This reactor provides a suitable environment for de-nitrification reactions to take place wherein dissolved nitrates are transformed into nitrogen gas. By using the nitrification mechanism, nitrates form in the aerobic reactor are converted to nitrogen gas. This reactor digests the sludge produced by the aerobic growth process in the aerobic reactor. The conversion of the biomass to methane gas is and indicator of three gas-forming events occurring inside the reactor. As a result, the creation of bubbles is frequent and a sign of a healthy reactor. Bacteria in this tank live in the absence of oxygen (Metcalf and Eddy, 2014).

- Aerobic reactor

Settled effluent from the anaerobic reactor is pumped to aerobic reactor that is also referred to as the mixed bed bioreactor (or MBBR) where the reactor is fitted with its own air blower and diffusers. The blower provides the air, which is subsequently diffused into the water. As long as the water's dissolved oxygen concentration is high, micro-bubbles increase the surface area between the air bubbles and the water mass, making it easier for bacteria and other microbes to absorb nutrients (Madan *et al*., 2022; Zhang *et al*., 2016). The oxygen uptake (or diffusion constant), which is influenced by the micro bubble size, is the most significant component that assures appropriate biological function in the reactor. Around 15-20% of oxygen is delivered (SEWTREAT, 2023)

Each bioreactor is filled with bioblocks to provide a media for the growth of bacterial colonies. This polyurethane construction gives bacteria and enzyme colonies a larger surface area to thrive on. Over a wide hydraulic range, the bio-blocks maximize oxygen transfer and hydraulic retention duration, which effectively reduces BOD and ammonia. The bio-blocks fill the reactor to a maximum of 60%. This makes it possible for the media to move about, removing any rate-limiting impacts that external diffusion would have on the reactor's efficiency (SEWTREAT, 2023).

- Clarification (Sedimentation)

Secondary settling takes place in the fourth phase. The so-called "sludge blanket" is made up of the cell material and settleable solids (of which the bacteria created for treatment in the previous two reactors). The procedure relies heavily on the sludge blanket. The primary settling tank (or anaerobic reactor) receives the blanket after it has thickened in order to "seed" or inoculate the raw sewage entering the plant and to initiate the denitrification process. This cycle is called the re-activated sludge cycle. The plant and process are more effective thanks to this technology. The performance of the clarifier is significantly affected by flow rate, particularly the up-flow rate. The sludge blanket suspension will lift to the height of the effluent pipe when up-flows are too high or the rate of sludge extraction is too low, producing poor plant effluent (Metcalf and Eddy, 2014).

### *III. Tertiary treatment*

Before the effluent is released into the receiving waterbody, the tertiary treatment, which includes the chemical treatment, simply adds another step to improve the effluent quality and eliminate impurities or any other pollutants (Hansen, 2015). Although tertiary treatments are relatively pricey, they can virtually eliminate all contaminants detected in wastewater. The most often employed techniques in the tertiary stage are the removal of nitrogen and phosphorus or chemical disinfection. Both phosphorus and nitrogen are successfully removed from the effluent using various chemicals. The purpose of disinfection, as the name implies, is to eliminate or inactivate pathogenic germs using chemicals like chlorine.

- Disinfection

Chlorine is a strong oxidizing agent that is widely utilized in pre-treatment oxidation and other oxidation and disinfection procedures, primary and secondary disinfection (USEPA, 2015). At this point, chlorine oxidants are used at the beginning in the process of treatment to control odor-causing compounds and reduce iron and manganese. Treatment facilities also use oxidants mostly in pre-treatment to induce inceptive disinfection of the water source as well as controlling biological growth on treatment basins and intake structures.

Source water variables conditions were discovered to alter the need for oxidants and when the concentration of source water for quality indicators like natural organic matter (NOM) increases, the NOM reacts with chlorine through oxidation, addition, and substitution to create DBPs. Abdullah *et al.*, (2009) found that in the pre-treatment, the creation of DBPs was vigorously influenced by the reactions of chlorine with inorganic and organic substances in the water supply.

The concerns of pre-treatment oxidation with chlorine include the lysing of algal cells which may cause algal toxins to be released (City and Marion, 2014). The algal toxins produced by specific algae from certain species of algae known as cyanobacteria, can affect the brain or liver as well as irritate the skin (Burtle, 2012). In oxidation processes, the chlorination of algal biomass may also result in creation of DBPs. The process of

oxidation can cause disturbance of algal cells causing the discharge of intercellular organic matter (IOM) into treated water (Wert, 2013; Mash *et al.*, 2014). IOM binding with utilized oxidants can be created to form DBPs.

Various studies have investigated chlorine dioxide ($ClO_2$) as a substitute disinfectant for chlorine in pre-treatment process. It was discovered that when $ClO_2$ is used in pre-treatment, it acts as a potent oxidant in pre- treatment delaying the addition of chlorine to a later stage of the treatment procedure (van Haute *et al.*, 2017; Jefri *et al.,* 2022). Additionally, this allows for lowering chlorine demand and possibility of chlorinated DBPs. The use of primary disinfection is the disinfectant in most cases, after the filtration process to attain a certain level of microbial inactivation (Davis and Shepherd, 2010). It has been discovered that this stage of disinfection is among the least effective followed by removal of particles by filtration and coagulation stages. During primary disinfection-chlorine or other primary disinfectants that are mostly commonly used such as chlorine dioxide, ozone, UV light and chloramines are employed to regulate microbial activity in treated water (USEPA, 2015).

The final effluent is ready for discharge at this point. To stop potentially dangerous or harmful microorganisms from entering the environment, the effluent is sterilized or disinfected. This is accomplished by adding chlorine to the water. The chemical doses at 95%, leaving a protective coating of disinfectant-containing residue in the water. The treated effluent can subsequently be released into receiving waterbodies which are typically rivers or ocean. Alternatively, it can be used for irrigation, toilet flushing or other non - portable purposes (SEWTREAT, 2023).

### 2.2.4. Chlorine chemistry and the importance of monitoring chlorine in wastewater

Chlorine is a commonly used disinfectant in water treatment as a chlorine gas ($Cl_2$), solutions of hypochlorite (NaOCl) or solid calcium hypochlorite powder ($Ca(ClO)_2$ often referred to as high test hypochlorite (HTH) (Brown, 2009; Madzivhandila and Chirwa, 2017; Zhang *et al.,* 2020). These forms of chlorine react with water according to the equations:

2.1 $Cl_2 + H_2O \leftrightarrow HOCl + HCl$

2.2 $NaOCl + H_2O \leftrightarrow HOCl + NaOH$

2.3 $Ca\ (OCl)_2 + 2H_2O \leftrightarrow Ca+ + 2HOCl + 2OH^-$

These compounds react with water to produce a weak acid known as hypochlorous acid (HOCl) which results in the formation of a toxic chlorine residual. The dissociation rate of HOCl depends on the pH of the water (Gile, 2016).

A study conducted by Netshidaulu, (2015) reveals that the chlorine demand is exacerbated by the formation of by-products resulting from the process of mixing raw water and the disinfectant. In sewage effluent, the formation of residual chlorine that destroys bacteria and prevents its regrowth is not as important as in drinking water treatment the distribution system must maintain a residual chlorine. Therefore, it is a waste to meet the need for chlorine in wastewater that is released into waterways.

Most wastewater treatments plants use physico-chemical processes to treat effluent from domestic and industrial sources. These processes comprise screening, grit removal, primary, secondary and tertiary treatment of waste effluent. Primary treatment covers the physical separation of solids that settle and float. The biological elimination of dissolved solids is a component of secondary treatment, and this has a lower chemical and energy requirement but removes aggregated suspended solids (Netshidaulu, 2015). This makes it an economical and ecologically sustainable approach to wastewater treatment (Wei *et al.,* 2018). Tertiary treatment involves physical, chemical, and biological treatment.

Abdullah *et al*., (2009) revealed that the chlorine demand increases with increasing density of $NH_3$-N, increased ultraviolet (UV) absorbance and pH in the source water. It is suggested that the facilities for drinking water utilizing surface water as a source experience seasonal variations in chlorine usage (Casey *et al*., 2012). Inflow water quality in water supply reservoirs is determined by seasonal variation, inflow water quality and in lake processes (Merz, 2013). Sediments, nutrients and other impurities can enter source through point and non-point source pollution which ultimately leads

to the influence of high chlorine demand in the source.

### 2.2.5. Environmental and health impacts of the presence of chlorine in water

Despite the importance of chlorination of water and sewage, exposure to chlorine has serious adverse effects. When chlorine is added to water, hypochlorous and hydrochloric acids are produced (Tak and Vellanki, 2018). Studies confirmed that chlorine exposure causes liver, bladder intestinal cancer; high blood pressure and allergies (Dehghani *et al.,* 2016; Azizl *et al.*, 2017; Lin *et al.*, 2022). According to Lin *et al*. (2013), liver cancer has also been associated with elevated levels of arsenic exposure in drinking water, albeit this effect was insignificant at exposure levels below

0.64 mg/L. Human body has chlorine as chloride whose deficiency in the body causes vomiting and diarrhea (Rolfes *et al.,* 2012). Chlorine is renowned for an irritating smell similar to that of bleached detergents, it is nonflammable, yet it is an explosive gas. Chlorine rapidly evaporates if exposed to organic and inorganic compounds. The solubility of chlorine in water and its interaction leads to the development of biological damage (Baker *et al.*, 2016)

The global "water crisis" is primarily driven by the limiting of the number of freshwater resources available to people and the ecosystem. Water pollution escalates the crisis and manifests itself by the degrading water quality (Aniyikaiye *et al.,* 2019). At any specific location along a river or water body, the water quality reflects significant anthropogenic inputs such as industrial and municipal wastes (Apeh, 2012; van der Laan *et al.,* 2012). Furthermore, according to the United Nations (2014), anthropogenic effect or combined natural and anthropogenic influences determine the quality of each water body.

Human health is impacted by the rise in bacterial infections and water-borne illnesses such as cholera and diarrhea. It is believed that these waterborne illnesses, particularly those that induce diarrhea, account for 3 to 5 million child deaths per year. These illnesses continue to be the leading course of water related illness worldwide and, along with a few others, are among the primary causes of death and disability worldwide (CSIR, 2010; Yang *et al.,* 2012). This is despite the significant

advancements in biomedical disciplines and public health initiatives that have made it simpler to control many infectious diseases over the past century. Yang *et al.,* (2012) reported that new and reemerging infectious illnesses have increased in prevalence and spread across the world.

Human health is significantly affected by exposure to unsafe water. For example, height loss in adults is associated with childhood exposure to pollution during critical growth phase (Zaveri *et al.,* 2020). A major contributor to childhood illnesses is water contamination. In 2016, 940,000 children globally lost their lives to pollution in the air, water, and soil, with 2/3 of those fatalities that happen to kids under the age of 5 (Landrigan *et al*., 2019). The bulk of these deaths happened in low- and middle-income nations. According to a study conducted in Bangladesh to evaluate the Kapotaksha River water pollution and its impacts on Human health & Environment in four selected areas (Barakpur, Srirampur, Prbazar, and Gouranandapur), river pollution causes many people to get scabies (Hanif *et al.,* 2020). Additionally, industrial water contamination is associated with skin cancer (Arif *et al.,* 2020).

Water contamination is a direct cause of many infectious disorders associated with diarrhea (Ahmed and Ismail, 2018). Drinking non-purified water contaminated with parasitic worms results in illnesses (Ansari and Akhmatov, 2020). For all ages, it was discovered that consuming purified water from water treatment plants decreased the incidence of diarrhea compared to untreated water (Clasen *et al*., 2015). There are numerous health hazards linked with chlorine, both in its molecular and compound forms. For example, most plant species die if exposed to a high concentration of chlorine/chloride due to the addition of hypochlorite to soil (Parveen *et al.,* 2022). On the other hand, human health is adversely affected by poor quality of drinking water. Water-borne illnesses in humans, for example, result from ingestion of drinking water of poor quality and this is a major concern in underdeveloped countries. The main driver of illness and mortality in emerging nations continues to be related to the detrimental impact of water contamination on health (Lin *et al.*, 2022)

Another source of exposure to chlorine disinfection by-products is swimming. According to Li *et al*., (2015), chlorination the most common way of disinfecting

swimming pool water. However, while bacteria are eliminated, DBPs are created. Therefore, swimming in chlorinated pools negatively impacts on health due to the DBPs exposure in addition to chlorinated water inducing cellular oxidative stress in living organisms. This has been demonstrated by studies on experimental rats' growth

and behavior which remained unaffected except after a 12-week program of swimming instruction in chlorinated water of a similar composition to that of public pools. The rats demonstrated deteriorating health and a decline in their metabolic profiles. Notably, the irritation associated with chlorinated water affects the eyes and skin more severely than the lungs. This suggested that training volume, intensity, and frequency may be the main causes of lung damage brought on by swimming. The liver is the organ that DBPs are most likely to attack among the body's five major organs (heart, liver, spleen, lungs, and kidneys) (Li *et al*., 2015).

Chlorine reacts with organic matter in the process of drinking water chemical treatment-which leads to the formation of DBPs that are known to cause adverse reproductive effects such as intrauterine growth, low birth weight and spontaneous abortion (Grellier *et al*., 2010; Wright *et al.*, 2017). Studies conducted by several researchers have found that the use of chlorinated water has adverse effects in humans such as increasing miscarriage, stillbirths as well fetal birth defects. Fetal birth defects such as heart and brain abnormalities as well as cancerous growths have been associated with the presence of chlorine in wastewater around the world (Costet, *et al.,* 2011; Lin *et al.*, 2022, Jaakkhola, 2007; Barrie, 2009; Mohsen *et al.,* 2019; Säve-Söderbergh, 2021).

Chorine naturally reacts with suspended organic matter such as decaying tree residue; animals remain to produce chlorinated hydrocarbons and THMs. These compounds are found mostly in water supply and are classified as the main cause of cancer (Mohsen *et al.,* 2019). Chlorine exposure increases due to some human activities such as swimming in chlorinated water and this is worsened by the production of chloroform due to an increase in water temperature. Concentrations of chloroform up to 7 mg/L have been reported to slow down blood flow in humans (Michaud *et al.*, 2007). Chlorine easily combines with natural organic matter that is brought into the water

through various media, including bathers, creating CBPs that are toxic. Diverse exposure pathways to chemicals in swimming pools (water ingestion, skin absorption, and inhalation) is influenced by the individual exposome. This increases the concentration of volatile CBPs in the water and air above the pool. As such swimming personnel for indoor swimming activities such swimming teachers, pool maintenance, personnel, and competitive swimmers are more susceptible to CBPs exposure from dissolved and volatile components. (Couto *et al.*, 2021). It has been found that extended swimming in indoor chlorinated pools aggravates asthma attacks on asthmatic swimmers (Bougault *et al*., 2012).

Chlorine can also be toxic to plants. According to Parveen *et al*., (2022), the DBPs produced by chlorine reactions with organic matter may have negative impacts on the microbes and plankton present in the ecosystems, as well as the flora and fauna of the receiving water body. However, chlorine use is indispensable for plant growth, and it influences mineral uptake by plants. Citrus plants have been shown to absorb less chlorine due to the higher relative abundance of calcium (as companion ion) in the soil layers deeper than 60 cm. The growing input of Cl-containing fertilizer under a mean annual rainfall of 1,474 mm, has been reported to raise the content of Cl in the soil and plant leaves. With respect to other cationic nutrients, chlorine considerably improved the N and K absorption, which in turn improved the flavor and juice yield of sweet oranges (Turhan, 2021). It also enhanced the yield (13.24-37.8 9%), fruit weight, and vitamin C (Vc) (Liu *et al.*, 2021). Notably, there are concerns that due to the continued use of sulfur-containing fertilizers in farming, the sulfur (S) could increase the likelihood for the formation of methylmercury (MeHg), a bioaccumulative neurotoxin. This could increase dietary exposure to MeHg on humans and animals (Lei *et al*., 2021). Further concerns emanate from the observed accelerated deposition of cadmium in the roots of crop plants due to sulfur, which reduced rice output (Fan *et al*., 2010).

For some plants, such as citrus, tobacco, and grape plants, which are referred to as "Cl sensitive crops," chlorine also manifests as a poisonous element (Xu *et al.*, 1999). Citrus yield decreased by 17%, trunk-diameter growth slowed down by 59% annually, and soil salinity linearly increased as a result of long-term irrigation with river water with

salt level that induced electrical conductivity of up to 2.5 $dS.m^{-1}$ (Prior *et al.*, 2007) Due to the unfavorable conditions and poor farming practices such as saline soils, decreased rainfall, excessive fertilizer use, and irrigation with saline water, it is simple to poison people and limit plant development. The safe dosage of Cl- containing fertilizers for this Cl-sensitive crop has not been established by farmers before. As a result, potassium sulfate ($K_2SO_4$), rather than potassium chloride (KCl), has long been used as a K fertilizer in China, where citrus is traditionally grown. Long- term use of $K_2SO_4$ has resulted in a sharp increase in soil sulfate ($SO_4^{2-}$), which has caused a severe acidification of the soil environment due the formation of weak sulfuric acid from the residual ($SO_4^{2-}$) (Tabak *et al*., 2020).

### 2.2.6. Legislation overview

Various ideas, including the preventative, polluter pay and precautionary principles, have emerged as a result of the development of international environmental regulations. Additionally, a monitoring instrument that aids in the application of the aforementioned principles is the Environmental Impact Assessment (EIA) (UNEP, 2015). Only a small number of nations and continents have laws that are specifically aimed at wastewater management; other nations have sectorial laws as well as general environmental laws while other nations have neither of these laws. As part of the Environmental Protection Act of 1970, which is also referred as the Code of Practice for Management of Domestic Wastewater, New Zealand is one of the nations that regulates wastewater. Only a small number of nations recognize the right to sanitation in their constitutions, compared to the number of nations that have recognized the right to water (including Bolivia, the Democratic Republic of Congo, Ecuador, Kenya, the Maldives, Nicaragua, Uruguay, and South Africa). The Safe Drinking Water Act (SDWA), which is known as the primary federal law that seeks to assure good quality drinking water in the United States, is an example of a national legislation. In addition, several other nations have similar laws that safeguard drinking water sources quality.

In South Africa, the hierarchy of environmental laws that also ensure that WWTPs are compliant and lessen their dangers to the environment and public health are founded

on a human rights perspective, which is accepted by the South African government. The National Environmental Management Act (NEMA)and the Constitution are the two main environmental legislation that control wastewater and water quality management in South Africa. The National Water Act, Water Services Act and national water policies and strategies which serve as the foundation for National Water Resource Strategy and the Target Water Quality Guidelines are examples of core sector specific legislation. Wastewater management is also indirectly supported by other health and local government rules.

Everyone has the right to sufficient access to water as stated in section 27 of the Republic of South Africa's constitution of 1996. Furthermore Section 24 upholds everyone's right to a healthy environment and requires it to be protected for current and future generations through appropriate legislative and other actions meant to stop pollution related to environmental damage. As a result, water restrictions are implemented in places with a lack of water and are based on population density and water levels in dams. These limitations are put in place to promote water conservation among communities and guarantee reliable supply (DWA, 2012).

By encouraging cooperative environmental governance NEMA established the legal foundation for implementing section 24 of the constitution. In addition to outlining important concepts like the polluters pay principle, precaution, sustainable development and environmental justice, it establishes rules for decision making and facilitates collaboration across governmental institutions. Furthermore, a duty of care is established by section 28 (1) of NEMA, which mandates that responsible parties take reasonable steps to prevent and remediate pollution and environmental harm. The Department of Water and Sanitation (DWS) directs and controls the water and sanitation industries in South Africa, creates strategy and policy, and supports the industry. DWS, which is in the process of incorporation, is governed by two Acts (DWS, 2018).

To address inequality in water access, two radical legislative frameworks have been developed: The goal of the Water Services Act and The National Water Act. The goal of the Water Services Act, No. 108 of 1997 (WSA 108 of 1997) is to provide every

person with access to basic sanitation and water supplies. The Act includes provisions for securing adequate water supplies and a healthy environment. The right to basic water supply and sanitation is outlined in Section 3 of the Act. National Water Act, no 36 of 1998, places a strong emphasis on preventing and reducing water pollution while ensuring the management, use and conservation of South Africa's water resources. A general duty of care is established by section 19 (1) which mandated that the landowners or anyone in charge of the land take reasonable steps to stop the occurrence, continuation or recurrence or contamination of water resources. According to Section 20 of NWA, Act no: 36 of 1998, water treatment plants must treat wastewater before disposal into the environment or water bodies, and they must have water use license for disposal. The discharge of water residue into water courses should be authorized according to Section 21(g) of the Act.

Both laws support the use of water to advance socioeconomic development and provide national authorities with a constitutional duty to set up a functional infrastructure for managing water resources. DWS fosters an environment that is favorable for the effective management and use of water resources through the enactment of these Acts, governance and regulatory frameworks, and national strategic objectives.

The National Water Resources Strategy's (NWRS) main objective is to make it easier to manage the nation's water resources. It establishes the foundation for using, enhancing, safeguarding, controlling, and managing water resources. The NWRS provides details on the aspects of managing water resources. The Target Water Quality Guidelines are the main source of information for establishing water quality standards for various applications and safeguarding the health of aquatic ecosystems, while the National Water Resources Strategy delineates the fundamental principles for water resource management in South Africa.

The National Health Act (Act 63 of 1977) (NHA) intends to provide policies for the improvement of the health of Republic of South Africa citizenry. According to Section 20(1), each local government must take all legal, necessary, and practically feasible steps to prevent any nuisance, unsanitary condition, or offensive situation. In addition,

the local authority is required to clean up any contaminated water before it is used by its residents, regardless of whether the water came from sources inside or outside of the district. Adequate supply of clean water is essential to the environment, health of living organisms and economy of the country, with 2.4% of freshwater from 70% of Earth's water however more than 60 billion of freshwater is yearly needed to manage annual world population growth (Choy *et al.*, 2014). It has been estimated that the world population will increase by 40%- 50% in the next 50 years, and it is anticipated that this will increase the water demand and have serious impacts on the environment (Krishnakumar *et al.*, 2017). Access to clean water in South Africa is a constitutional right of every person (Mckenzie, 2012)

The division of duties between district and local municipalities is outlined in the Local Government; Municipal Structure Act (Act 117 of 1998). District municipalities are tasked with overseeing residential wastewater and sewage disposal system under section 84 (1). Section 55(1) of the Municipal Systems Act (Act 32 of 2000) states that the provision of services to the local community in a sustainable and equitable manner is the responsibility and accountability of the municipal manager who serves as the head of administration in accordance with the policy directives of the municipal council. Additionally, among other things, the primary services that must be offered by towns include the supply of clean water, sanitation, and garbage removal.

The Acts on water quality are just one example of how well South Africa has done in developing laws and supporting legal instruments. It has also done a great job of relating its sanitation and wastewater management laws and policies to human rights, water and the environment. SA is regarded as a pioneer in wastewater treatment research and development when compared to other nations (UNEP, 2015).

DWS launched the Green Drop Programme in 2008 in response to the various difficulties encountered in putting all the aforementioned enforcement methods into practice. Instead of enforcing compliance through strict regulations, an incentive-based program seeks to encourage conformity through motivation and rewards. DWS has concluded that rewarding positive behavior is more effective and efficient than punishing undesirable behavior (DWA, 2013b). Wastewater Service Institutions

performance is evaluated by the green-drop assessment process, which then awards or penalizes the institution based on proof of its success or shortcomings in relation to the Green Drop Key Performance Areas (DWA, 2011).

In South Africa, wastewater treatment plant performance is now estimated using two assessment schemes: the Cumulative Risk Assessment and the Green Drop Assessment. The Cumulative Risk Assessment concentrates on the wastewater treatment function, whereas the Green Drop Assessment examines the wastewater business' whole value chain (reticulation, pumping, treatment, and discharge) within the municipal (or other) wastewater services industry. The latter strategy gives the regulator knowledge about the municipal business' treatment division, which is one of the wastewater value chain's high-risk segments (DWS, 2017; Ntombela *et al.,* 2016). Through these tools, municipalities in South Africa can identify important risk areas in their wastewater systems and prioritize taking appropriate action to address them because to risk- based regulation (DWA, 2011). When a municipality's WWTP scores ≥90% on the green- drop assessment Key Performance Areas, it will be

granted green drop status. A wastewater system is in a critical state and performing exceptionally poorly if its score is less than 30% (DWA, 2013a, 2013b; Ntombela *et al.,* 2016).

### 2.2.7. Knowledge gap and Way- Forward

Despite the study's effectiveness in establishing connections between physicochemical characteristics, chlorine demand, and microbiological contamination, the study did not completely account for treatment performance at the process level meaning that the precise steps in the wastewater treatment plant responsible for inadequate removal of organic and nutrient loads were not determined. This makes it more difficult to determine whether inefficiencies result from primary, secondary, or tertiary treatment failures. Although significant statistical correlations were found, the study did not provide causal processes that explain why these associations arise under operational conditions. This is particularly important for variables that showed mixed association patterns, such as phosphate and chloride. Advanced

microbiological evaluations beyond *E. coli*, such as viral or protozoan indicators, which are frequently crucial for determining public health hazards in treated effluent, were not included in the study. Although seasonal variability was taken into account, hydraulic loading effects and short-term operational changes were not thoroughly investigated. Future studies should concentrate on evaluating wastewater treatment performance in a more comprehensive and process-based manner. To enable focused operational improvements, this involves determining which treatment phases are mostly to blame for increased COD, ammonia, phosphate, and microbial loads. To provide a more thorough evaluation of the dangers to public health associated with effluent discharge, future research should extend microbiological investigation beyond *E. coli* to include pathogenic bacteria, viruses, and protozoa. Future research should investigate sophisticated nutrient removal techniques such membrane filtration, biological nutrient removal (BNR), or artificial wetlands to address nutrient pollution, especially in plants with persistently high phosphate and ammonia levels. To assess treatment effectiveness and environmental toxicity issues, long-term monitoring of chlorine residuals and disinfection by-products (DBPs) is required. To ascertain the true environmental impact, this should be connected to ecological evaluations of receiving water bodies.

## 2.3. Summary/ Conclusion

The literature shows that inorganic and organic pollutants such as ammonia, nitrate, phosphate, suspended solids, and COD are important factors that affect wastewater quality and treatment effectiveness. These compounds increase chlorine demand, reducing the effectiveness of disinfection by limiting free chlorine available. By decreasing the amount of free chlorine that is accessible, these substances raise the demand for chlorine, which lowers the efficacy of disinfection. To eliminate contaminants and reduce the amount of chlorine used, effective wastewater treatment depends on primary, secondary, and tertiary processes operating as intended. However, total performance might be jeopardized by inefficiencies at any level. Continuous monitoring is necessary to guarantee successful disinfection and reduce hazardous disinfection by-products (DBPs) because chlorine behavior in wastewater is impacted by variables such as pH, temperature, and reactive chemicals. Although

chlorine is essential for eliminating pathogens, inappropriate use puts aquatic ecosystems and human health at risk. As a result, strong regulatory frameworks and balanced disinfection procedures are required, along with efficient implementation and monitoring. In general, literature emphasizes the necessity of integrated strategies that connect environmental preservation, treatment effectiveness, and water quality management.

# CHAPTER 3

# Research design and methods

## 3.1. Introduction

This chapter describes the area of the study, its design and how the data was obtained. It describes the sampling frame, techniques that were used to sample and how the data was analyzed. The limitations of the study, data validity, research plan and ethical clearance are discussed. The parameters that are analyzed are pH, EC, ammonia, nitrate, phosphate, COD, chloride, and total and fecal coliform bacteria.

The effluent contains organic and inorganic compounds that impact disinfection. temperature, pH, organic matter, turbidity, and other factors can all affect the inactivation efficiency. The resistance characteristics of microorganisms and other influencing factors should be considered when selecting disinfection technologies for the drinking water and wastewater treatment processes (Kong *et al.,* 2021). The effluent temperature also determines the effect of disinfection. Temperatures above room temperature usually increase certain chemical reactions' speed in effluent and this decreases disinfection. The disinfectant may disintegrate or volatilize at higher temperatures, which can also reduce disinfection (Okpara *et al.,* 2011). For the same inactivation, a smaller dose is required at higher temperatures (Kong *et al.,* 2021).

## 3.2. Study location map

Hebron Mall Wastewater Treatment Plant (WWTP), run by SEWTREAT, is situated in Hebron, close to the North-West Province and Gauteng borders, approximately 30 km northwest of Pretoria (**Figure 3.1**). To support regional water management initiatives, the plant mainly handles wastewater from Hebron Mall. The plant treats wastewater and releases the treated effluent into the Apies River, a tributary of the Pienaar River, with a daily treatment capacity of about 5 megaliters (ML). An essential biological resource that promotes biodiversity in the area is the Apies River. The Hebron Mall WWTP is in the Tshwane Metropolitan Municipality, Gauteng Province, South Africa and is a component of a quaternary catchment that contributes to regional hydrology.

The facility can be found about at latitude -25.6116° and longitude 28.1791°.

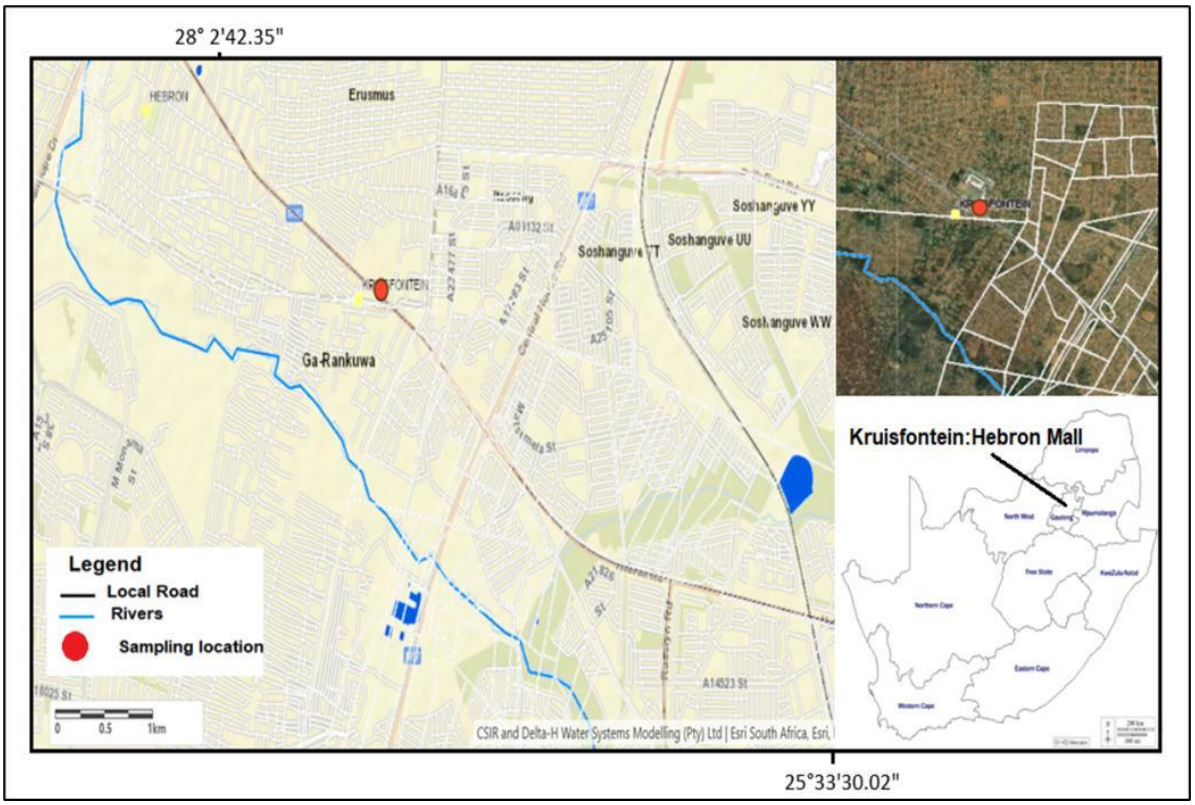


*Figure 3.1: Location of the WWTP (Arc GIS, 2010).*

## 3.3. Research method

The study is a quantitative research approach because it involves experiment, numerical data, and descriptive statistics. Pearson's Correlation analysis and linear regression analysis were used for analyzing data.

## 3.4. Research approach

This study examines the effects of both organic and inorganic substances on the demand for chlorine in a WWTP using a quantitative experimental technique. The methodology consists of field sampling, laboratory analysis, and statistical evaluation to determine the correlations between chlorine demand, chlorine residual, and physicochemical and microbiological parameters. This method combines correlation

analysis and seasonal sampling to offer a thorough understanding of chlorine behavior in wastewater disinfection procedures.

## 3.5. Sample and data collection

Data was collected as primary data by means of sampling influent and effluent at the treatment plant. Water sampling was done in all four seasons (September 2023- July 2024) with triplicate results. For the sampling session, 1 L of effluent from inlet/ raw and final was collected into sterilized quartz bottles and transported in ice chest kept at a 4 °C to Waterlab (Pty) Ltd for analysis. Regarding the control samples, quartz bottles were preserved before sampling. Collection of water samples was done early in the morning between 6 am and 8 am. Collected water samples were subsequently taken to the laboratory within three hours of collection.

## 3.6. Data analysis method

### 3.6.1. Laboratory analysis

Water samples were taken to the laboratory for analysis. Water parameters that were analyzed are residual chlorine, pH, ammonia, electrical conductivity (EC), temperature, nitrate, phosphate, chloride, chemical oxygen demand (COD), suspended solids (SS) and *Escherichia coli*. The results of the parameters were compared with the national standard guidelines (WHO, 2007).

#### *I. pH and Temperature*

The pH and temperature were analyzed on site using the HANNA HI9146 Dissolved Oxygen Meter (HANNA Instruments, Johannesburg, South Africa), South African National Standard Determination of pH. SANS 5011:2005 procedure was followed. Each measurement was accomplished by immersing the cell in the samples and readings were allowed to stabilize prior to recording of results. The cell was rinsed with distilled water, shaken to remove internal droplets, and then wiped outside prior to insertion into the following sample to eliminate possible cross contamination between samples. Normal pH ranges between 5.5 - 7.5.

The basicity and acidity of water are shown by the pH readings. High pH levels in the WWTP indicate the presence of ions, which include hydroxide, carbonates and chlorine during treatment (Wen *et al*., 2020; Leopold and Freese, 2009).

### *II. Electrical conductivity*

The widespread determination handheld conductivity HANNA HI9146 Dissolved Oxygen Meter was used to measure the conductivity of samples following the manufacturer's instructions and standard method SANS 7888:2005. Each measurement was carried out by immersing the probe into the sample. The readings were allowed to stabilize before results were recorded. It is measured in mS/m.

### *III. Nitrate, Ammonia and Phosphate*

For nitrate analysis, 10 mL of water sample was poured into a test cell, followed by the addition of a nitrate reagent sachet. The cell was capped and shaken vigorously for about 5 minutes to ensure complete dissolution and reaction of the sample. The sample was then inserted into a Palintest Photometer 7500 (Palintest, Kingsway, United Kingdom), and the nitrate concentration was measured following the instrument instruction. For ammonia determination, 10 mL of sample was transferred into a test cell and ammonia reagent sachet was added. The mixture was shaken for approximately 5 minutes to allow full color development. The sample was then analyzed using the same spectrophotometric instrument. For phosphate analysis, 1 mL of the sample was diluted with 9 mL of distilled water in a test cuvette. A phosphate reagent sachet was added, and the solution was mixed thoroughly. Phosphate was measured using the same photometric technique for nitrate and ammonia analyses following spectrophotometric instrument manual.

### *IV. Chloride*

A 10 mL sample was placed into a test tube, and a chloride tablet was added to the tube. The mixture was shaken for 5 min to ensure proper mixing. It was then left for 30 min to dissolve before being analyzed using a Palintest Interface Photometer 7500 to obtain the results.

### *V. Chlorine, residual*

Chlorine residual was determined using a CHEMATEST 35 pocket colorimeter Instrument (SWAN Analytics, Hinwil, Switzerland). The concentration of chlorine was determined by the DPD free and total chlorine methods.

### *VI. Bacterial wastewater quality analysis (E. coli)*

Analysis of bacterial parameters was done in sterile containers within six hours of the samples being collected, followed by the Colilert -18 method for *E coli* analysis. About 100 mL of WWTP samples were added into a Colilert media and mixed until completely dissolved. The water sample was agitated to guarantee homogeneity before one packet of Colilert-18 reagent was introduced for Quanti-Tray (MPN) analysis. After fully mixing the sample, it was transferred into a Quanti-Tray/2000 and sealed using a Quanti-Tray Sealer. After that, the samples were incubated for 24 hours at 35°C. The samples were examined to establish whether *E. coli* was present after incubation. The sample remained colorless and non-fluorescent in the case of a negative result, but fluorescence under UV light or a change in color to yellow indicated a positive result. The procedure followed manufacturer's standard method which is in compliance with international standards for testing the microbiological quality of water ISO 9308-2 (ISO, 2012). The number of positive wells in the Quanti-Tray that displayed color change or fluorescence during incubation was tallied using the MPN (Most Probable Number) approach. We next estimated the Most Probable Number of *E. coli* per 100 mL of the sample using the MPN table (Venkateswaran *et al*., 1996)

### *VII. Total suspended solids*

Total suspended solids (TSS) were analyzed using a gravimetric method in accordance with solids analysis standard procedures. An analytical balance was used to record the initial masses of pre-weighed filter papers after they had been dried. A filtering device was then used to filter each well mixed sample through the prepared filter paper. After filtration, the filter papers with the retained solids were dried for about two hours at 103–105 °C in an oven to eliminate moisture. In order to stop the filters from absorbing moisture from the ambient, they were then moved to a desiccator to

cool for fifteen minutes. The final mass was then determined by reweighing the cooled filter sheets.

The concentration of suspended solids was analyzed as the difference between the final and initial masses of the filter paper, which represents the mass of solids retained during filtration. This gravimetric method is based on the idea that the mass differential before and after filtering can be used to determine the amount of suspended matter in a sample, American Public Health Association (APHA), 2017).

### *VIII. Chemical Oxygen Demand (COD)*

Chemical oxygen demand (COD) was analyzed using the closed reflux colorimetric method (Method 8000) in compliance with standard wastewater procedures analysis. 2 mL of a sample was poured into a pre-prepared COD digestion vial containing the necessary chemicals. A COD reactor was then used to digest the sealed vials for two hours at 150 °C. The vials were taken out after digestion and allowed to cool to room temperature for about 30 minutes. A spectrophotometer was then used to detect the absorbance of the digested samples, and COD values were determined immediately from the instrument calibration. Standard colorimetric techniques were used in the process to determine COD.

### *IX. Chlorine demand calculations*

Chlorine demand calculations:

$$Cl_{2\ demand}\left(\frac{mg}{L}\right) = Cl_{2\ dose}\left(\frac{mg}{L}\right) - Cl_{2\ residuals}(mg/L) \qquad \textit{Equation 3.1}$$

Colorimetric-photometric techniques may become useless if chlorine concentrations are above the tested limit. In the DPD method, for instance, over-range chlorine concentrations cause the reactant to turn brown or yellowish-brown; in these situations, the water sample needs to be diluted to fall within the measuring method's useful range. The concentration of the diluted material and the multiple of dilution can then be used to compute accurate findings (Patnaik, 2017).

## 3.6.2. Statistical analysis

Statistical analyses were performed using IBM SPSS Statistics. Pearson's correlation coefficient (r) was calculated to assess the strength and direction of correlation among the measured physico-chemical parameters. Statistical significance was assessed using p-values, with a threshold of $p \leq 0.05$ considered indicative of a statistically significant correlation. P-values were used to measure statistical significance; an association was deemed statistically significant if $p \leq 0.05$. Linear regression analysis was used to examine the link between dependent and independent variables. This method allowed for the quantification of the degree of connection between one or more independent factors and the prediction of the dependent variable. These statistical methods are suitable for determining important factors influencing the response variable and evaluating the interactions between environmental variables.

### 3.7. Validity and reliability

The instruments were calibrated as per the instructions, methods used were validated and verified. Regression analysis model was used to quantitatively analyze the reaction and effect of inorganic and organic compounds on chlorine demand in wastewater plants. The compounds are regarded as independent variables and chlorine demand as a dependent variable. Linear regression model was established to analyze quantitatively the relationship between independent and dependent variables (Fan, 2014).

### 3.8. Limitations of the study

There was insufficient literature related to the study, and it was difficult to benchmark the study with the previous studies.

### 3.9. Ethical consideration

The study required ethical clearance in accordance with UNISA research ethics requirements to obtain ethics clearance, though the study was not harmful to people and animals but proof for ethical clearance was needed for collecting water samples from the treatment plant and in the laboratory for analyses. Analyzed results shall be used for the purpose of the study only and shall be confidential.

# CHAPTER 4

# Results and discussion

## 4.1. Introduction

The findings from the data gathered during laboratory analysis are presented in this chapter. The results, which are the main conclusions of the investigation, are based on the physicochemical assessment and bacteriological assessment of WWTP. These findings address the research questions. Based on the several seasons that were sampled during the year, the results are described. Winter, Autumn, Spring and Summer.

## 4.2. Physicochemical assessment

The physicochemical parameters recorded for the sampling points are presented below and the sampling period commenced from September 2023 – July 2024. The World Health Organization (WHO) established limits were compared to the results obtained using the techniques described in chapter 3. The samples were tested triplicate for each season to ensure accuracy of the results.

### 4.2.1. Temperature

Temperature influences chemical processes, aquatic life, and water appropriateness, making it one of the key indicators of water quality. The effectiveness of chlorine disinfection diminishes as the temperature drops (Page *et al*., 2009). **Figure 4.1** shows how the temperature at the WWTP varies each season. The results are presented using bar graphs to show seasonal concentrations i.e., summer, autumn, winter and spring. The overall temperature for the sampling period of the influent ranged between

19.17 °C - 24.97 °C and for effluent ranged between 17.67 °C - 23.83 °C thus indicating a slight temperature drop between the effluent. The recorded values and the values (16.9–25.3 °C) reported by Olabode *et al*., (2020) were quite comparable. The lowest temperature (17.67 °C) was obtained in Winter, while the highest temperature (24.97 °C) was obtained in summer

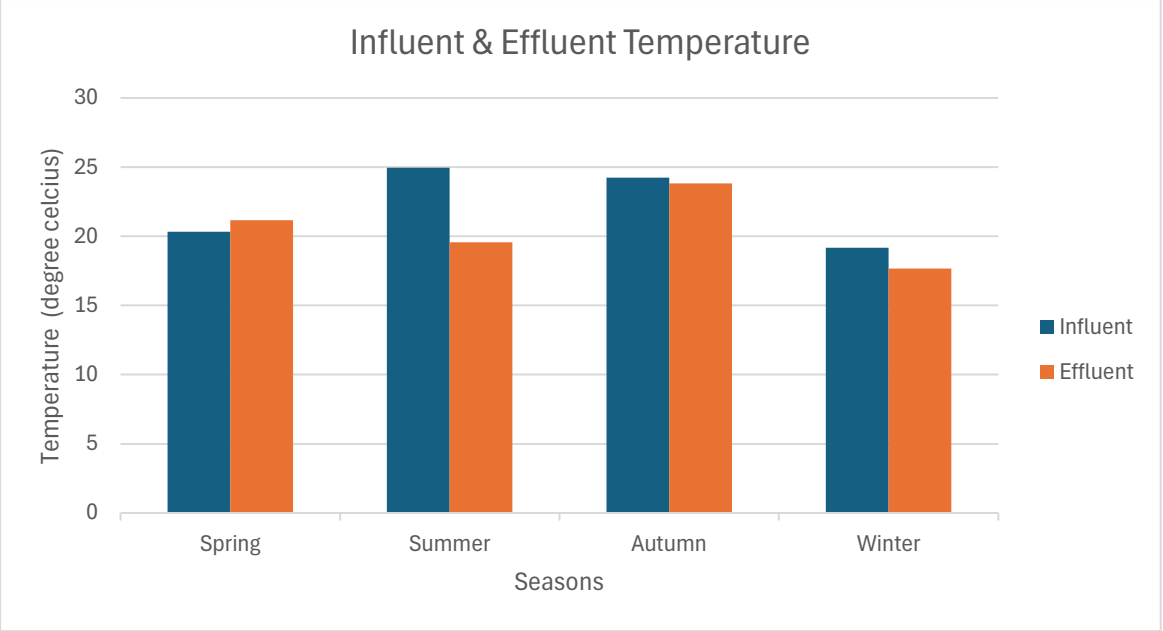


*Figure 4.1: Seasonal variation in temperature for WWTP (September 2023 to July 2024).*

In spring the temperatures ranged between (20.33 – 21.17 °C) and continued increasing in summer (24.97 °C) for influent and slightly decrease in effluent (19.57 °C) which indicates the effective treatment. It slightly decreases from summer to autumn (24.23 °C - 23.83 °C) which is due to no rainfall and intensity of sunlight. Lowest temperatures were observed in Winter ranging between (19.17 – 17.67 °C), while in spring there was a slight increase in temperature. The highest temperatures were observed in summer (24.97 °C) influent and autumn (23.83 °C) effluent. The most efficient reduction occurs in the summer, whereas an increase in effluent temperature relative to influent temperature occurs in the spring. This implies that the temperature is significantly influenced by seasonal variations. The effluent's temperature met the WHO guidelines for release of effluent into waterbodies. The receiving water body does not seem to be in danger due to the effluent temperature, according to these guidelines.

### 4.2.2. pH

The results for the seasonal variation in pH for the WWTP for the sample period is presented in **Figure 4.2**. The pH level of water determines its suitability for various uses and is recognized to affect the concentration of micronutrients, trace, and heavy

metals in the water (Agoro *et al*., 2018). The spring, summer, and autumn seasons had pH values that were roughly neutral (pH 7) and did not differ much from one another. The overall pH for all seasons ranges between (6.62 - 7.15) influent and (6.96 - 7.37) effluent. The lowest pH (6.62) was observed in spring while the highest (7.37) was observed in summer. The effluent is always greater than influent, regardless of the season. This suggests that the medium may be neutralized or somewhat alkalized by the WWTP system. The highest values occur in the summer, possibly as a result of temperature-influenced chemical processes or increased biological activity. The somewhat lower numbers in the spring and winter indicate less activity or input changes.

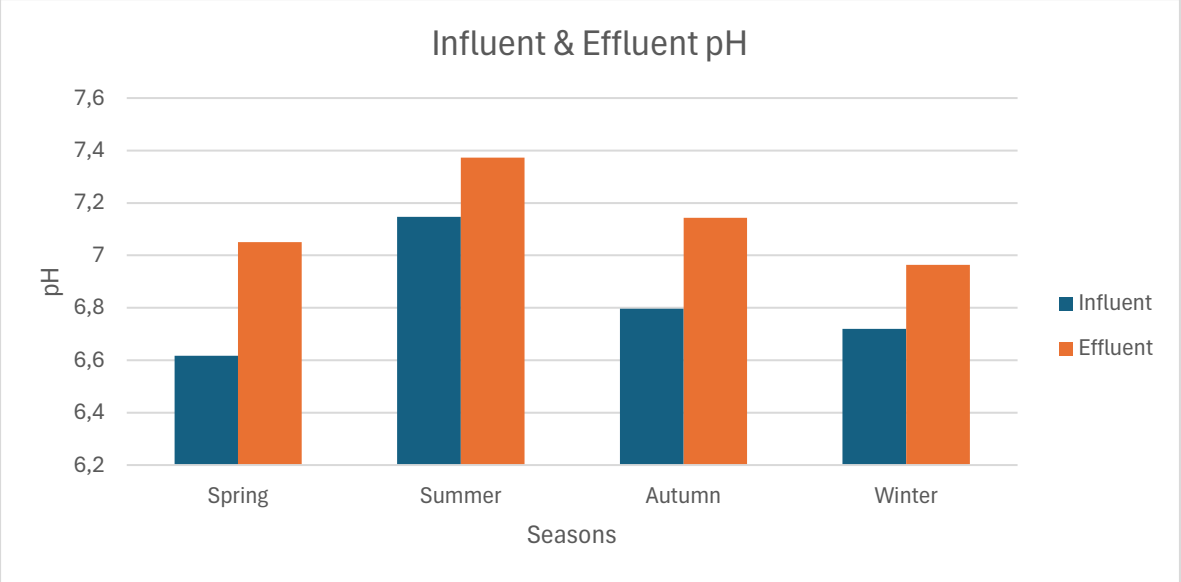


*Figure 4.2: Seasonal variation in pH for WWTP (September 2023 to July 2024).*

In spring the values ranged between (6.62 - 7.05), which indicates that the effluent value is somewhat higher, suggesting a mild rise. This could indicate that the effluent has undergone minor alkalinity alterations. In summer the values range from (7.15 - 7.37), despite a modest increase in the effluent, both fall into the slightly alkaline range. The system's chemical reactions or higher temperatures may have an impact on this. In autumn season the values range between (6.80 - 7.14), maintaining a neutral to slightly alkaline state, a little increase in the effluent is noted. In winter both readings (6.72 6.96) stay near neutral, with the effluent slightly rising, most likely as a result of

treatment processes being impacted by lower temperatures. This indicates that the water has been disinfected, and it may be the result of microbial decomposition of organic debris and bicarbonate, carbonate, and hydroxide produced by $CO_2$ (Baharvand and Daneshvar, 2019). Similar findings were made at the Deoli Bhorus Dam, where it was claimed that variations in pH are all reliant on the water's photosynthetic activity, which affects the water's $CO_2$, carbonate, and bicarbonate levels (Kalwale and Savale, 2012). The high amounts of carbonate used in the treatment process may have contributed to the pH trends that Olabode *et al*., (2020) reported, which tended towards alkalinity. The pH values observed for all sampling seasons for the effluent ranged between 6.96 – 7.37 which were all within the limits for discharge of effluent into the environments from WHO and this suggests that the effluent has no detrimental effect on the watercourse.

### 4.2.3. Electrical conductivity

According to Agoro *et al*., (2018), the EC is mostly ascribed to dissolved ions derived from broken-down plant matter and serves as a crucial gauge of surface water salinity. The results of the seasonal variation in EC of the WWTP is presented in **Figure 4.3** below. Over the course of the sampling period, the EC values for effluent seemed to be consistent and ranging between 130.7 – 410.3 µS/cm, for influent range between610.3 – 1015 µS/cm which were significantly greater.

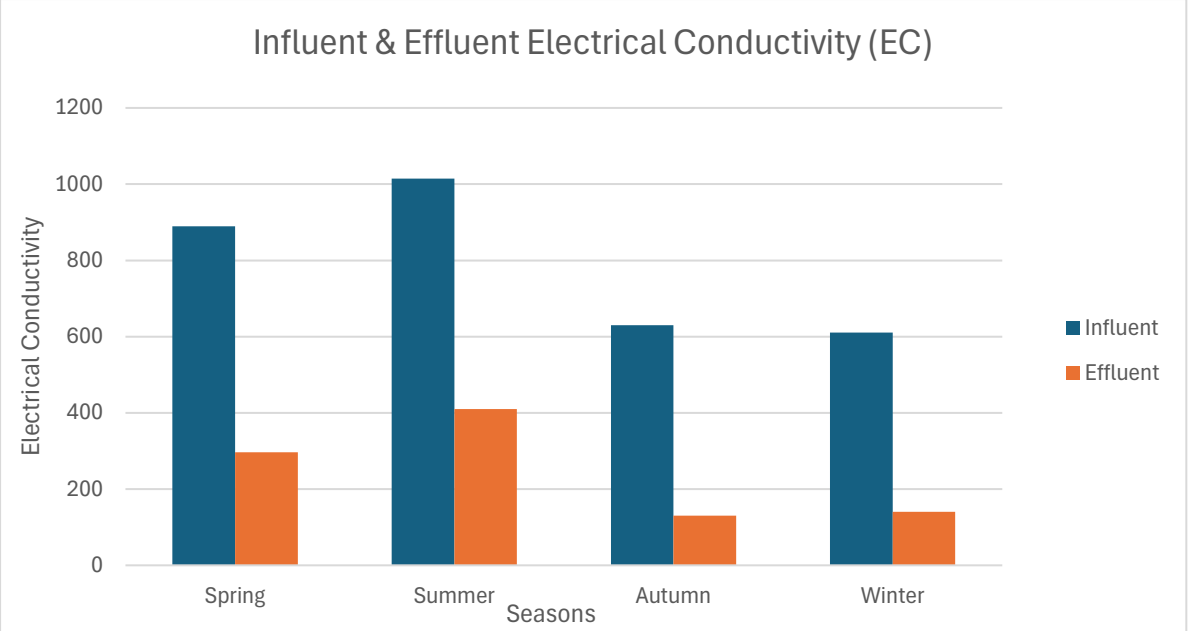


*Figure 4.3: Seasonal variation in EC for WWTP (September 2023 to July 2024).*

High EC readings in wastewater indicate a higher concentration of total dissolved solids. An increase in EC values indicates that there are a lot of dissolved, ionized inorganic compounds present. The rise in EC was also influenced by a high quantity of chlorine (Mamba *et al*., 2009). It was observed that influent always recorded higher EC values than effluent, high values were recorded in summer (1015 µS/cm) and the lowest values were recorded in winter for influent (610.3 µS/cm), while for effluent high values were recorded in summer (410.3 µS/cm) and lower values in autumn (130.6 µS/cm). Therefore, it is possible that additional undiscovered pollutants enter the plant during the spring and summer seasons, which is consistent with a similar pattern seen in two distinct studies on WWTPs and rivers (Osode and Okoh 2009; Agoro *et al*., 2018).

The highest values for the sampling points were observed in the spring (296.67) and summer (410.33), while the lowest values were observed in the autumn (130.67) and winter (140). The seasons with the highest treatment efficiencies, autumn (79.26%) and winter (77.06%), show robust system functioning. The lowest efficiency (59.57%) occurs in the summer, most likely because of high influent loads that exceed capacity. Spring achieves a higher percentage reduction because of its lower influent load, even though summer and spring have equal reduction values. This is consistent with other

reports that suggest seasonal and temperature variation affecting EC (Olabode *et al*., 2020). Furthermore, the influent values were too high, indicating that the WWTP is effective in reducing EC when compared to the effluent values. Standards were within WHO (1000 µS/cm) however only summer values for influent were above the acceptable limit.

### 4.2.4. Nitrate

The results for the seasonal variation in nitrate for the WWTP for the sample period is presented in **Figure 4.4**. The range for nitrate in influent ranges between (15.80 - 26.17 mg/L), exceeding the acceptable limit while in effluent ranges between (0.16 – 19.50 mg/L). The values obtained for effluents in summer, autumn and winter ranged (0.16 – 7.40 mg/L) fell within the recommended limits of 15 mg/L by WHO and the values recorded for spring (19.50) exceed the recommended guidelines for nitrate. Similar research conducted by (Ewemoje and Ihuoma., 2014) revealed that surface water sewage discharge significantly contributes to the decline in ecosystem health.

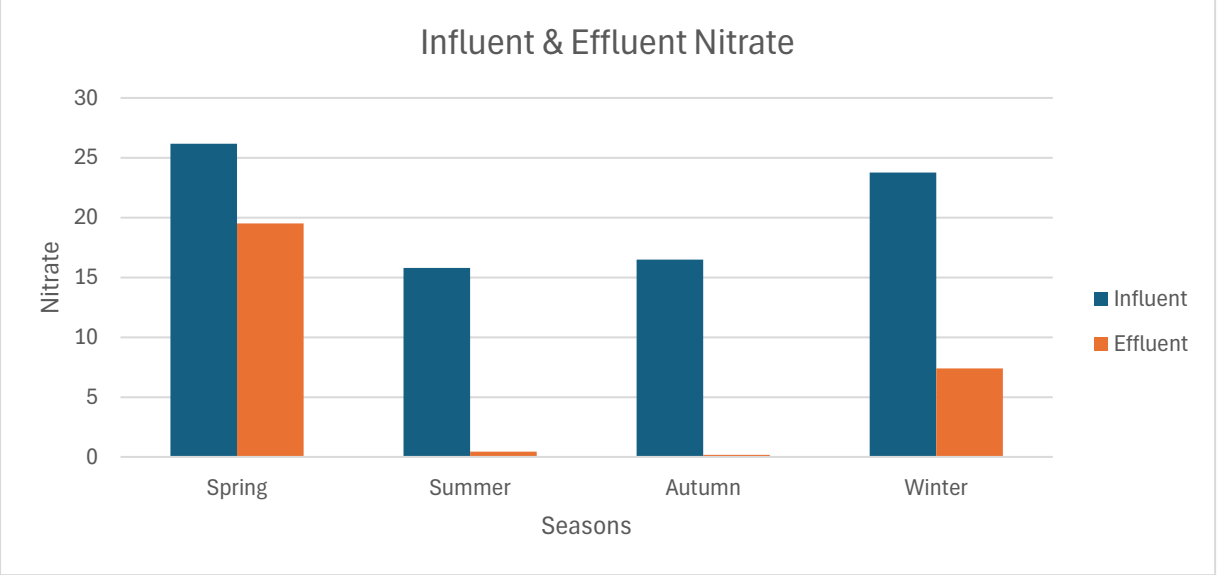


*Figure 4.4: Seasonal variation in Nitrate for WWTP (September 2023 to July 2024).*

With the lowest effluent concentrations and the highest treatment efficiency, autumn (99.01%) and summer (97.28%) demonstrate outstanding performance. The efficiency is lowest in the spring (25.50%), indicating difficulties in reducing pollutants. While

winter outperforms spring, it is not as good as summer or autumn. Seasonally, the concentrations of influent are highest in the spring (26.17 mg/L) and lowest in the summer (15.8 mg/L). It has been found that nitrate can cause eutrophication even at low quantities less than 1 mg/L (Mook *et al*., 2012; Ragheb., 2013), it can have an adverse effect on aquatic life, reduce biodiversity, and produce unpleasant odors, making the water unsuitable for recreational purposes (Akan *et al*., 2007; Roshvanlo *et al*., 2014). Higher summer and autumn treatment efficiency removes more pollutants, which lowers the requirement for chlorine. Higher chlorine demand is caused by microbial activity and leftover organic matter in spring and winter, when treatment effectiveness is lower.

### 4.2.5. Ammonia

**Figure 4.5** below shows the results of the seasonal variation in ammonia ($NH_3$) for the WWTP for the sample period. The WWTP in the influent ranges between (27.17–101.43 mg/L) while in the effluent ranges between (1.09 - 28.00 mg/L). Winter has the lowest effluent concentration (1.09 mg/L) and the highest efficiency. This exceptional performance is probably a result of the low influent concentration (27.17 mg/L), as the system runs well within capacity. Autumn has the highest concentration (28 .00 mg/L) of effluent.

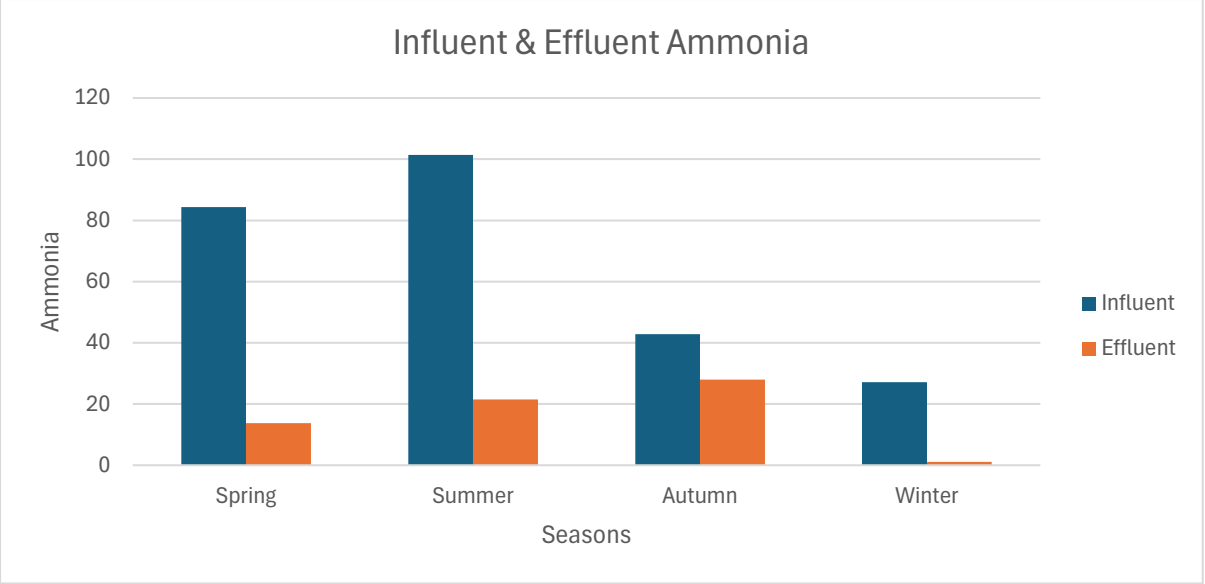


*Figure 4.5: Seasonal variation in $NH_3$ for WWTP (September 2023 to July 2024).*

The highest influent concentration (101.43 mg/L) is in summer due to increased pollutant loading, the lowest in winter (27.17 mg/L) likely from reduced activities and spring and autumn are moderate. The lowest effluent concentration (1.09 mg/L) is in winter indicating high treatment efficiency, followed by autumn (28 mg/L) reflecting reduced treatment efficiency and spring and summer are moderate. Winter has the highest effluent efficiency reduced from (27.17 - 1.09 mg/L) while autumn has a lowest efficiency reduced from (42.83 – 28 mg/L) however spring and summer has moderate efficiency.

High ammonium concentrations in water may result from fertilizer runoff, sewage, or industrial waste (Makarovsky *et al*, 2008). Extreme acute exposure to ammonia gas can result in serious respiratory tissue damage, which can be lethal or cause severe pulmonary impairment that frequently necessitates the use of a mechanical ventilator or, in rare cases, lung transplantation (Pangen *et al*., 2022; Maries and Maries., 2018). Ammonia damages animal body tissue by creating ammonium ions through an exothermic reaction with bodily tissues, liquefactive necrosis, and deeper burns. Therefore, exposure to ammonia gas can harm the mucosa, leave scars, or even puncture the skin, eyes, lungs, and digestive tract (Pangen *et al*., 2022).

With almost total pollution elimination, winter (96.01%) performs the best. The least

efficient season is autumn (34.62%), when effluent concentrations are high, and reduction is restricted. The influent concentration is lowest in winter (27.17 mg/L) and highest in summer (101.43 mg/L). Although summer is marginally less effective because of its increased influent load, both spring and summer exhibit excellent treatment effectiveness. The results meet the limits by WHO, therefore, the discharged effluent is safe for the environment and aquatic life in water bodies. WWTP samples for winter and spring were within the WHO recommended limit of 15 mg/L and summer, and autumn were above the recommended WHO limit. Lower ammonia levels in winter and spring result in a higher free chlorine requirement because of increased microbial activity and organic matter breakdown, which raises chlorine demand. High ammonia levels in summer and autumn increase chloramine formation, which lowers free chlorine but stabilizes overall demand.

According to Paul (2017), depending on the level of fecal contamination, both breakpoint chlorination and chloramination at low chlorine-to-ammonia ratios can be useful for disinfection at low ammonia concentrations ($\leq$ 0.5 mg/L). In these circumstances, breakpoint chlorination is usually more appropriate. Properly adjusting chlorine dosage based on initial ammonia levels and overall water quality is essential for disinfection effectiveness and regulatory compliance. High and hazardous ammonia levels draw attention to the possibility of environmental damage and emphasize the necessity of sophisticated nitrogen removal techniques in wastewater treatment (Atwebembeire *et al.,* 2019).

### 4.2.6. Phosphate

Since phosphorus is thought to be the main source of eutrophication in aquatic ecosystems, where higher nutrient concentrations result in higher primary productivity, it is an essential parameter (Benit and Roslin, 2015). The results of the seasonal variation in phosphate ($PO_4^{3-}$) for the WWTP for the sample period is presented in **Figure 4.6** below. The concentrations varied from (44.8 – 80.7 mg/L) for influent and (7.9 – 11.5 mg/L) for effluent. The highest influent level (80.67 mg/L) was in winter; indicating that the increased pollutant load is possibly from runoff or other seasonal activities. The lowest influent levels (44.7 - 45.6 mg/L) were in summer and autumn,

suggesting reduced pollutant inputs while spring (56.13 mg/L) shows moderate influent levels. The wintertime phosphate content varies greatly, as can be seen from this. The results observed for effluent were not significantly different from the concentration in other seasons.

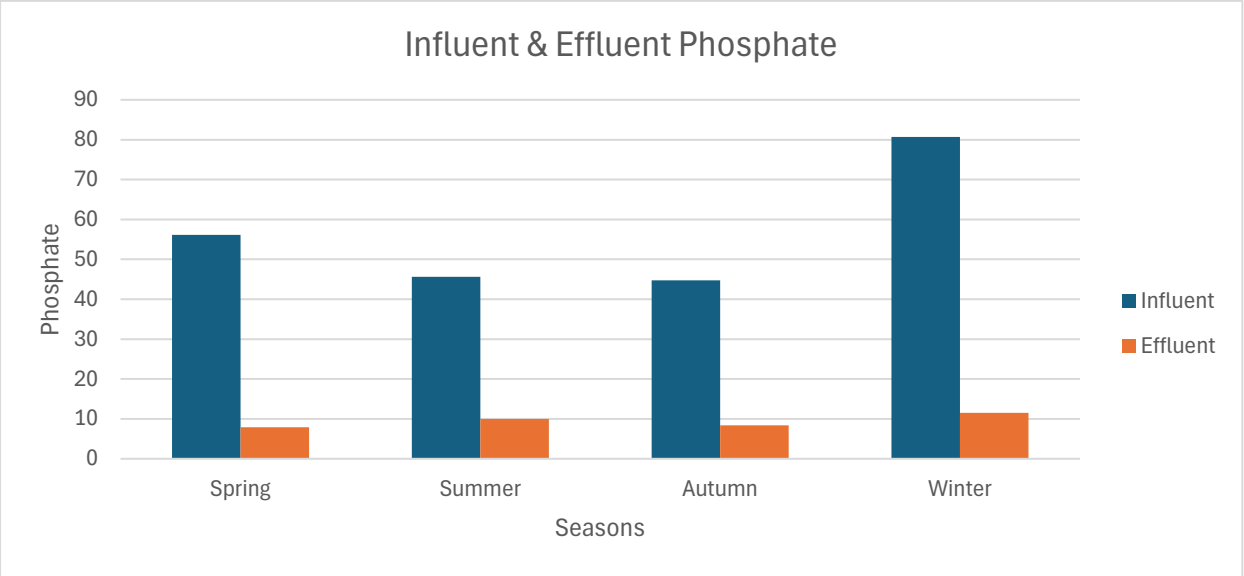


*Figure 4.6: Seasonal variation in ($PO_4^{3-}$) for WWTP (September 2023 to July 2024).*

The highest level of effluent (11.52 mg/L) was observed in winter reflecting the lowest treatment efficiency due to increased influent volume. The lowest level of effluent (7.94 mg/L) was in spring with the treatment efficiencies of approximately 74.3% and 74.8% respectively suggesting better treatment performance for the season. Summer and autumn show moderate effluent values (8.40 – 9.98 mg/L). The wintertime phosphate content varies greatly, as can be seen from this. The results observed for effluent were not significantly different from the concentration in other seasons.

The concentrations of phosphate range obtained in effluent was more consistent within the sampling period level as shown in **Figure 4.6** above. The concentrations for influent (44.76 mg/L) in autumn and effluent (7.94 mg/L) in summer were very low and a sudden rise in ($PO_4^{3-}$) concentration occurred in winter. This can be linked to excessive detergent waste disposal from the mall and effluent food and meat processing establishments. Shrestha and Kazama, (2007) found that the increase in phosphate concentration can be linked to the overuse of fertilizers in agriculture, the

waste from food and meat processing companies, and the improper disposal of detergent waste by families. The phosphate concentrations in the WWTP comply with the WHO set limit of 10 mg/L except winter season (11.52 mg/L). High phosphate and nitrate concentrations have been linked to increased eutrophication in aquatic environments, which raises oxygen demand and can result in several undesirable ecological issues (Agoro *et al*., 2018; Paltahe *et al.,* 2018). Increased organic matter, microbial growth, and DBP generation are all consequences of high phosphate concentrations, which also increase the demand for chlorine. In winter (0.47 mg/L), when phosphate levels surpass WHO guidelines, this effect is most noticeable, highlighting the necessity of efficient fertilizer removal in wastewater treatment. A crucial trade-off between chemical safety and microbiological stability in water distribution systems is highlighted by the fact that phosphate-based corrosion inhibitors can lessen the production of DBP but may also increase microbial release and chlorine consumption (Shi *et al.,* 2022).

Phosphorus is always discharged into wastewater treatment plant effluent by a wide range of sources (Yamashita and Yamamoto-Ikemoto, 2014). The presence of phosphorus compounds in discharged wastewater is attributed to the fact that it is not completely precipitated. Furthermore, between 20 and 30% of phosphorus is eliminated by primary and secondary wastewater treatment processes, leaving the remainder in the wastewater (Ruzhitskaya and Gogina, 2017).

### 4.2.7. Chloride

The seasonal variation of chloride ions ($Cl^-$) in WWTP within the sampling period is illustrated in **Figure 4.7** below. The chloride concentration for influent ranged between

57.38 – 289.12 mg/L while for effluent ranged between 33.03 – 103.47 mg/L. The highest influent (289.12 mg/L) was observed in winter, suggesting a significant increase in pollutant load resulting in a treatment efficiency of approximately 64.2%, followed by summer (115.12 mg/L) indicating elevated pollutant loading indicating an even higher pollutant loading yielding a lower efficiency of about 32.0%. The values recorded in spring (58.63 mg/L) and autumn (57.38 mg/L) have comparatively

moderate levels.

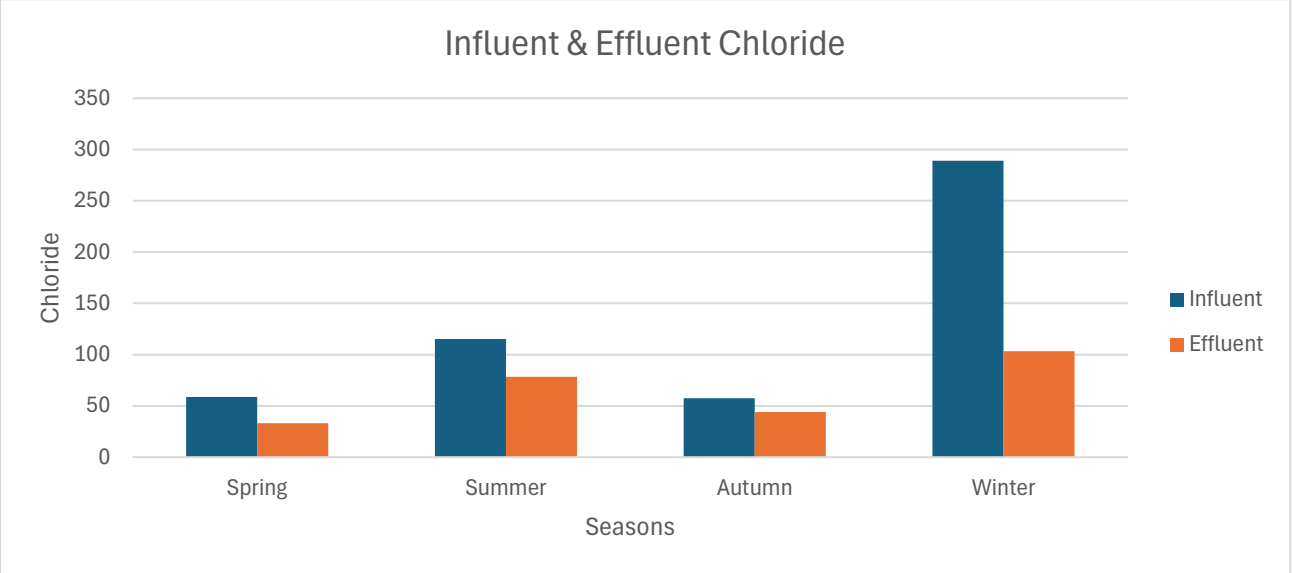


*Figure 4.7: Seasonal variations in Chloride for WWTP (September 2023 to July 2024).*

The highest effluent (103.47 mg/L) was observed in winter reflecting a considerable number of pollutants, followed by summer (78.27 mg/L) that indicates lower treatment efficiency. The results for spring (33.03 mg/L) and autumn (43.91 mg/L) reflect moderate values of effluent compared to other seasons. Autumn indicating the lowest removal efficiency among the seasons at roughly 23.4% while spring exhibits comparatively higher efficiency at approximately 43.6%, with influent reduced from

58.63 to 33.03 mg/L compared to all the seasons. The chloride concentration recorded in WWTP complies with the recommended limit by WHO (100 mg/L). The plant's values exceeded 3.25 – 224 mg/L recorded by Agoro *et al.,* (2018), but they fell short of the 127.72 – 396.16 mg/L reported by Iram and associates from wastewater effluents from Pakistan's Kohe-Noor textile and Nul Lah Lai (Iram *et al.,* 2013).

Treatment has an impact on the concentration of chloride because sodium chloride, which is found in food and human dietary sources, passes through the digestive system unaltered in wastewater. Water starts to taste salty at concentrations over 250 mg/L, becomes disagreeable as the level rises, and possibly makes freshwater unfit for irrigation in agriculture (Chigor *et al.* 2013). Owing to the effect of high chloride

content on some aquatic animals' growth and reproduction, it poses a risk to species survival in an aquatic ecosystem by threatening the sustainability of ecological food sources (Aniyikaye *et al*., 2019). Since high chloride levels affect disinfection effectiveness, contribute to organic load, and encourage the production of DBP, they raise the demand for chlorine. In autumn and winter, when environmental factors cause greater organic breakdown and less chlorine effectiveness, this effect is more noticeable. The National Water and Sewerage Corporation's use of reactive chemicals, such as chlorine, to purge water of harmful bacteria during water treatment is probably the cause of the increased chloride levels in sewage effluents (WHO, 2011).

### 4.2.8. Residual chlorine

**Figure 4.8** below shows the results for residual chlorine. The recorded results are for effluent only because there is no dosage of chlorine in the inlet of the WWTP. The WWTP effluent ranges between 0.37 mg/L (summer), 0.11 mg/L (autumn), 0.03 mg/L (winter) and 0.17 mg/L (spring) respectively.

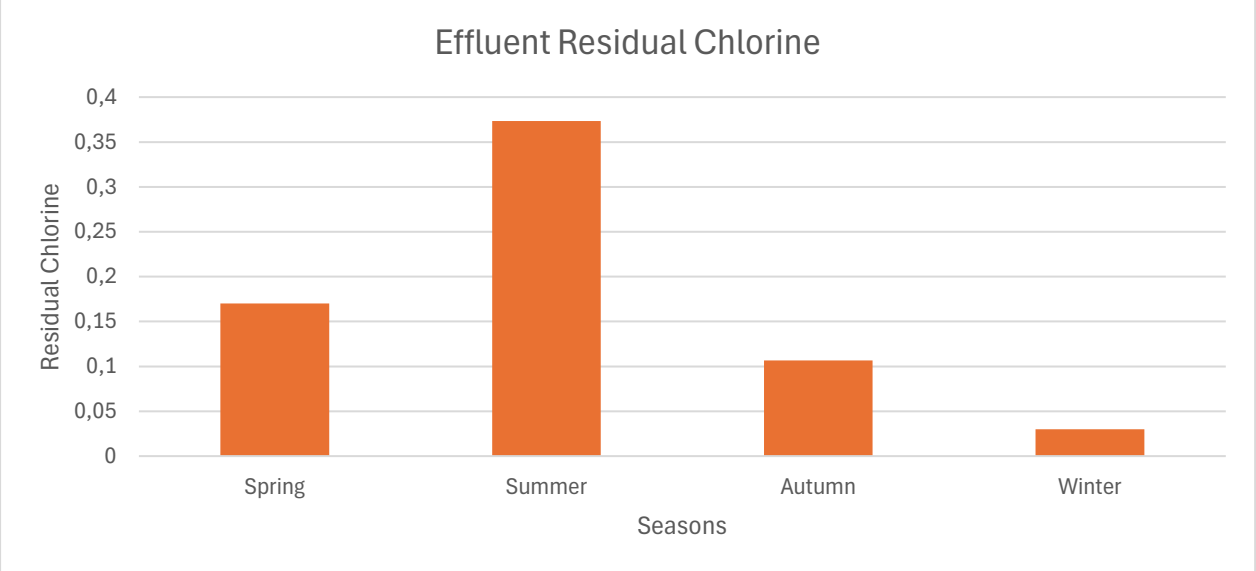


*Figure 4.8: Seasonal variation in free chlorine for WWTP (September 2023 to July 2024).*

After peaking in the summer (0.37 mg/L) suggesting a chlorine retention efficiency of

approximately 74.6%, the parameter declines in the spring (0.17 mg/L) and autumn (0.11 mg/L) with retention efficiency of approximately 40% and 60% respectively, before falling to its lowest point in the winter (0.03 mg/L) showing that just 6.0% of the chlorine was still accessible. According to these results, there is a noticeable seasonal change, with the parameter being most active or abundant in the summer and least active in the winter. Environmental elements such as warmer temperatures could be the cause of the summer peak. Possibly reflecting the end of the summer peak season as environmental conditions deteriorate, the value drops dramatically in autumn.

Low chlorine demand (0.13 mg/L) and high residual chlorine (0.37 mg/L) in summer imply that environmental conditions such as warmer temperatures result in decreased chlorine consumption, perhaps because of less interaction with pollutants or lower organic loads. Greater chlorine demand (0.47 mg/L) and low residual chlorine (0.03 mg/L) in winter show that more chlorine is being used up, most likely because of greater reaction rates with pollutants, more organic matter, or slower chlorine disinfection caused by colder water. As the temperature decreases in spring, more chlorine is used, as seen by the autumn in residual chlorine (0.11 mg/L) and the rise in chlorine demand (0.39 mg/L). Similarly, as the season transitions to summer, residual chlorine begins to rise once more in the spring (0.17 mg/L) while chlorine demand falls (0.33 mg/L).

The results show an inverse connection between residual chlorine and chlorine demand. Chlorine consumption rises from summer (0.13 mg/L) to winter (0.47 mg/L), whereas residual chlorine levels fall from summer (0.37 mg/L) to winter (0.03 mg/L). This implies that more chlorine is used up during the winter months before it can be left as a residual. This is probably because there is more organic matter present, microbiological activity is higher, or chemical reactions raise chlorine consumption. Chlorine demand and residual chlorine seem to be influenced by seasonal variations in temperature and organic matter, with increased demand during the colder months resulting in lower residual levels. Similar results were found by Dyck *et al.,* (2015), where winter had the most residual chlorine, whereas spring and summer had the least.

### 4.2.9. *E. coli*

The effluent values gradually drop from spring to winter. Spring (4907.33 MPN/100 mL) has the greatest value, followed by summer (4849.33 MPN/100 mL), autumn (4548.67 MPN/100 mL), and winter (4472.67 MPN/100 mL) (**Figure 4.9**). This suggests that during the year, the measured metric has been trending downward with concentrations showing a progressive seasonal decline from spring to winter, representing a gradual reduction of approximately 8.8%. The results for influent were>100000 MPN/100 mL for all seasons.

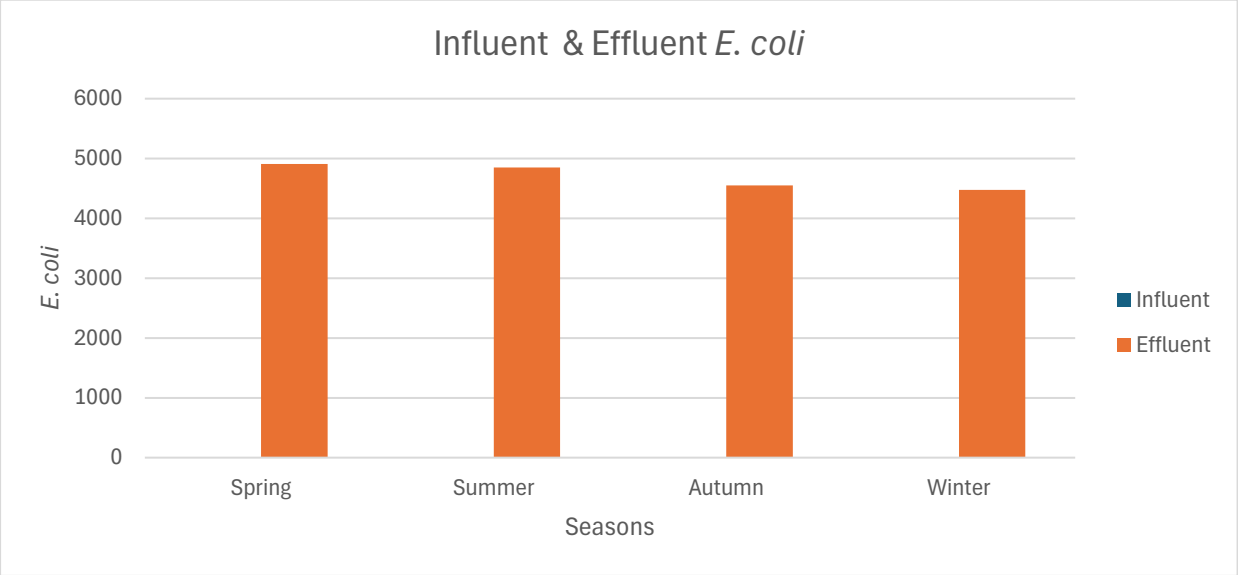


*Figure 4.9: Seasonal variation in E. coli for WWTP (September 2023 to July 2024).*

The *E. coli* is most prominent during the spring, as indicated by the greatest value, which could be the result of favorable environmental circumstances, increased biological activity, or resource availability. The lowest value in winter denotes less activity, which may be caused by natural processes becoming dormant, colder temperatures, or less sunlight. The findings show seasonal variation, with spring and summer being the busiest or most productive seasons.

Every wastewater sample that was examined had a higher total and faecal coliform count (MPN/100 mL) than the WHO recommended threshold of ≤1.0 $\times 10^3$ MPN/100 mL. These findings showed that using wastewater to irrigate crops is not a good idea.

This included using wastewater to irrigate public parks and sports fields as well as to grow vegetables such as cucumber, lettuce, and salads that people could eat directly. Fecal coliform results are consistent with those of a previous study (Al-Jasser, 2011), which examined wastewater samples from an effluent treatment plant in Riyadh, Saudi Arabia. The mean fecal coliform value (geometric) for this reported study was 7.1 × $10^1$ MPN/100 mL – significantly lower than the current study findings. Given that untreated wastewater is being released into surface water bodies during this investigation, the variation in the fecal coliform count may be related to the treatment plant's effectiveness. About half of the wastewater samples under study conducted by (Tariq, *et al.,* 2020) had fecal coliform and *Escherichia coli* contamination. The discharge of extremely polluted wastewater in and around KSK city indirectly poses serious risks to human health and environmental contamination.

### 4.2.10. Total suspended solids (SS)

**Figure 4.10** present the seasonal variations in the concentrations of SS for influent and effluent at WWTP. The WWTP in the influent ranges between (124.8 – 186.53), while in the effluent ranges between (42.4 – 84.53).

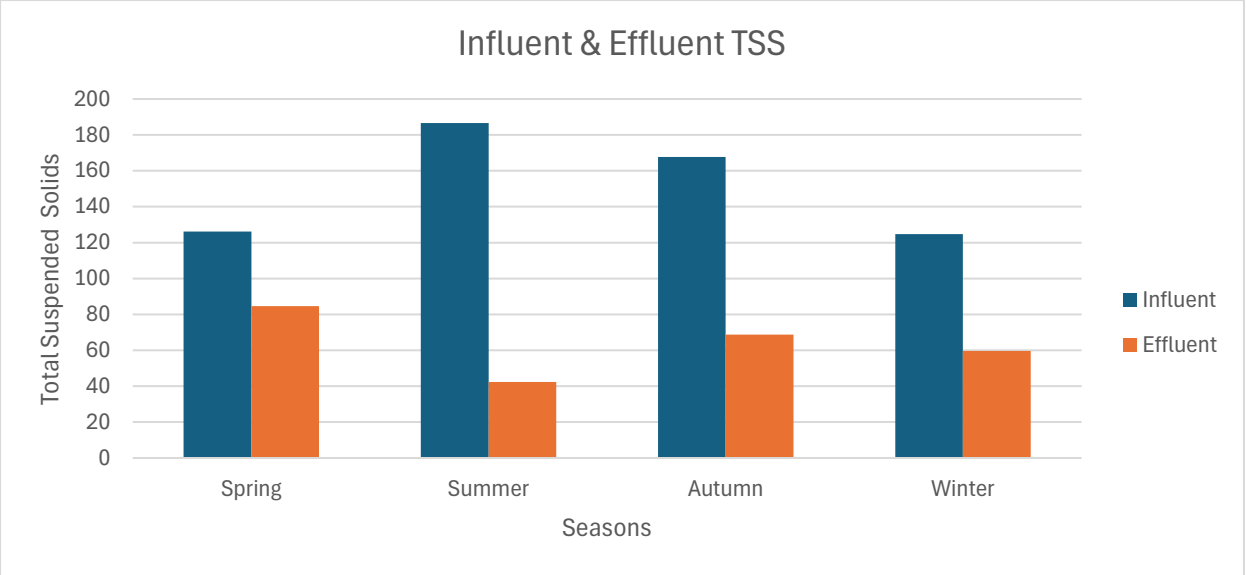


*Figure 4.10: Seasonal variation in TSS for WWTP (September 2023 to July 2024).*

The highest SS in the influent (186.53 mg/L) was observed in summer, followed by

autumn (167.63 mg/L) which may result from seasonal runoff. In comparison to summer and autumn, spring (126.13) and winter (124.8 mg/L) have comparable and lower influent levels, which may be due to fewer pollution inputs. The highest SS in the effluent (84.53 mg/L) was observed in spring, suggesting lower efficiency treatment while the lowest effluent SS level (42.4 mg/L) was observed in summer reflecting the most effective treatment. The autumn effluent SS level (68.73 mg/L) and winter (59.6 mg/L) demonstrate a moderate effluent value compared to other seasons. The most efficient season is summer, when influent drops from 186.53 - 42.4 mg/L which is 77% reduction and spring has the lowest efficiency, with influent falling from 126.13 to 84.53 mg/L (33% drop).

The results meet the limits by WHO therefore the discharged effluent is safe for the environment and aquatic life in water bodies. The high amount of TSS indicates that suspended solids interference may make treatment processes including coagulation, filtration, and disinfection for ingestion difficult (Salaudeen *et al*., 2019). Increased chlorine demand is correlated with high TSS levels because more chlorine is consumed in the reaction with organic matter and suspended particles before disinfection can take place.

### 4.2.11. Chemical Oxygen Demand

COD is known as the concentration of strong oxidant needed to decompose both organic and inorganic materials (Chigor *et al*., 2013). When determining the amount of organic matter in wastewater samples, COD is a test that can be used instead of BOD. The COD test measures the amount of industrial and household pollutants in wastewater. It calculates the amount of oxygen required for organic matter to oxidize in water under specific oxidizing agent (often potassium dichromate) and temperature (150 °C) conditions for two hours (Kale and Bandela, 2016). The results of the seasonal variation in COD are presented in **Figure 4.11** below. The range of COD for the sampling period ranges between 54.67 – 346 mg/L where high values were found at the influent.

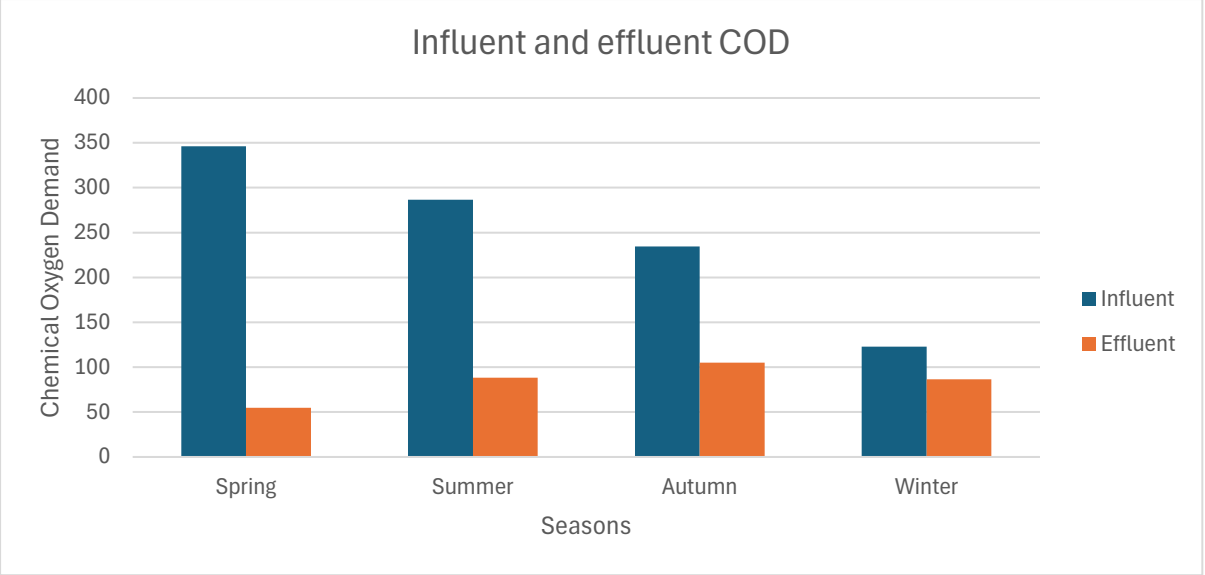


*Figure 4.11: Seasonal variation in COD for WWTP (September 2023 to July 2024).*

The highest influent level (346 mg/L) was observed in spring, indicating significant pollutant loading, followed by summer (286.67 mg/L). Autumn demonstrates a moderate influent level (234.67 mg/L) and the lowest influent level (123 mg/L) was observed in winter. The highest effluent level (97 mg/L) was recorded in autumn suggesting reduced treatment efficiency and the lowest effluent level (54.67 mg/L) was recorded on spring. Similar effluent levels are shown in the summer (88.33 mg/L) and winter (86.67 mg/L), with moderate treatment performance in comparison to other seasons. The best results are obtained in the spring (346–54.67 mg/L), indicating that the treatment is effective during this season (84.2% reduction) and Wintertime had the lowest efficiency (123–86.67 mg/L), a 29.6% decrease, indicating difficulties with treatment performance during this time of year.

Since organic compounds in water resist microbial oxidation, COD readings are often greater than BOD values (Aniyikaiye *et al*., 2019; Baharvand and Daneshvar 2019). According to Odjadjare and Okoh, (2009) and Agoro *et al*., (2018) Both organic and inorganic compounds with oxygen-demanding properties are the source of the high COD levels found in wastewater. Aquatic life is greatly impacted by high BOD and COD levels in the water, which also drastically reduce oxygen levels. Elevated COD levels in water could indicate substandard water quality brought on by farmland or urban effluent outflows (Anderson and Grether.,2010), which could lead to increased

oxygen depletion that impacts aquatic life (Salequzzaman *et al*., 2008).

Throughout all sampling seasons, the recorded data indicated that the WWTP effluent met the WHO-established COD limits of ≤100 mg/L. However, seasonal variation may have contributed to autumn COD readings (105 mg/L) being above the permissible limit. Furthermore, the effluent's high COD value suggests that seasonal changes have left some components resistant to microbial decomposition, which could have a negative impact on the receiving water body. An excessively high concentration of COD suggests that the effluent may contain harmful substances that are immune to microbial breakdown and pose a risk to receiving water bodies (Paltahe *et al*., 2018).

### 4.2.12. Chlorine demand calculations

**Table 4.1** below shows that more chlorine was overwhelmed in summer season as the average was above all the seasons (0.37 mg/L), however more chlorine demand was observed in winter season (0.47 mg/L). A chlorine dosage is represented by the constant value of 0.5 mg/L. Figure 4.12 shows seasonal variation in chlorine demand for the WWTP. Since all seasonal values fall below this cutoff, it's possible that the parameter does not consistently reach critical levels. Similar results were observed by (Netshidaulu, 2015) the warm season usually affects a higher chlorine application. The requirement for higher chlorine dosages arises from diminished disinfection caused by environmental exposure. On the other hand, it's also possible that the chlorination system was not operated and controlled properly.

*Table 4.1: Chlorine demand for the WWTP Seasonal monitored effluent quality data.*

| **Season** | **Mean Chlorine residual ($Cl_2$) mg/L** | **Chlorine dose mg/L** | **Mean $Cl_2$ demand** |
|---|---|---|---|
| Spring | 0.17 | 0.5 | 0.33 |
| Summer | 0.37 | 0.5 | 0.13 |
| Autumn | 0.11 | 0.5 | 0.39 |
| Winter | 0.03 | 0.5 | 0.47 |

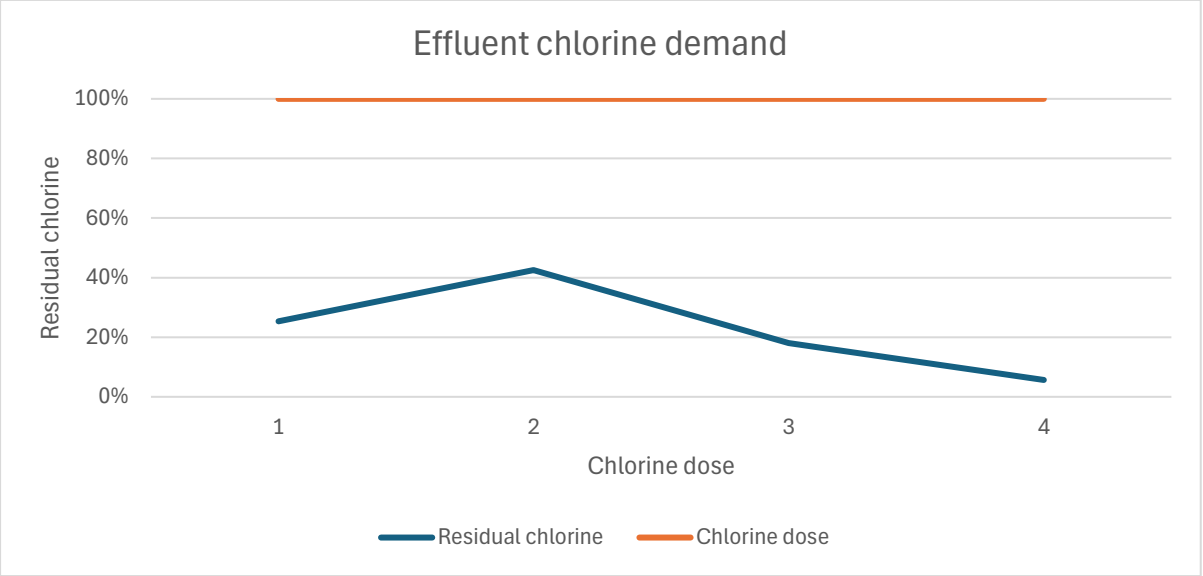


*Figure 4.12: Seasonal variation in chlorine demand for WWTP (September 2023 to July 2024).*

## 4.3. Mean and standard deviation values of the physicochemical parameters

**Table 4.2** below provides additional information on the mean values of the physicochemical characteristics. According to the investigation, high mean values and standard deviations for indicators such as phosphate, ammonia, COD, and EC point

to possible pollution influencing the quality of the water. Significant oscillations in indicators such as ammonia, phosphate, and chloride are probably caused by different seasonal changes. On the other hand, temperature and pH exhibit little fluctuations, indicating stable conditions that are less affected by pollution incidents. High levels of ammonia, nitrate, suspended particles, and *E. coli* indicate contamination.

*Table 4.2: Mean and Standard deviation for influent and effluent.*

| **Parameters** | **Influent** | | **Effluent** | |
|---|---|---|---|---|
| | **Mean** | **Std. Deviation** | **Mean** | **Std. Deviation** |
| | | | | |
| **pH** | 6.82 | 0.25027 | 7.1325 | 0.2801 |
| **EC** | 786.17 | 183.512 | 244.42 | 121.966 |
| **Nitrate** | 20.558 | 5.0228 | 6.8742 | 8.74259 |
| **COD** | 247.58 | 88.557 | 81.67 | 18.312 |
| **SS** | 151.28 | 52.438 | 63.817 | 26.2053 |
| **Ammonia** | 63.933 | 31.8952 | 16.08 | 11.40063 |
| **Phosphate** | 56.792 | 17.6583 | 9.4633 | 2.47766 |
| **Temperature** | 22.175 | 2.856 | 20.558 | 2.5614 |
| **Chloride** | 130.06 | 116.70723 | 64.6683 | 31.19585 |
| ***E. coli*** | | | 4694.5 | 196.719 |
| **Residual chlorine** | | | 0.17 | 0.13685 |
| **Chlorine demand** | | | 0.33 | 0.13685 |

*Table 4.3: Correlations Analysis of the physicochemical parameters (SPSS).*

| | | pH | EC | Nitrate | COD | SS | Ammonia | Phosphate | Temperature | Chloride |
|---|---|---|---|---|---|---|---|---|---|---|
| pH | Pearson Correlation | 1 | .414 | -.623* | .117 | .383 | .376 | -.562 | .585* | .033 |
| | Sig. (2-tailed) | | .181 | .031 | .717 | .219 | .229 | .057 | .046 | .920 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| EC | Pearson Correlation | .414 | 1 | -.187 | .738** | .168 | .965** | -.347 | .379 | -.299 |
| | Sig. (2-tailed) | .181 | | .561 | .006 | .602 | <.001 | .270 | .224 | .346 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| Nitrate | Pearson Correlation | -.623* | -.187 | 1 | -.043 | -.414 | -.193 | .469 | -.828** | .158 |
| | Sig. (2-tailed) | .031 | .561 | | .894 | .181 | .547 | .124 | <.001 | .624 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| COD | Pearson Correlation | .117 | .738** | -.043 | 1 | .182 | .811** | -.611* | .353 | -.688* |

| | | pH | EC | Nitrate | COD | SS | Ammonia | Phosphate | Temperature | Chloride |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sig. (2-tailed) | .717 | .006 | .894 | | .571 | .001 | .035 | .261 | .013 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| SS | Pearson Correlation | .383 | .168 | -.414 | .182 | 1 | .178 | -.466 | .613* | -.327 |
| | Sig. (2-tailed) | .219 | .602 | .181 | .571 | | .579 | .127 | .034 | .299 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| Ammonia | Pearson Correlation | .376 | .965** | -.193 | .811** | .178 | 1 | -.467 | .374 | -.457 |
| | Sig. (2-tailed) | .229 | <.001 | .547 | .001 | .579 | | .125 | .231 | .135 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| Phosphate | Pearson Correlation | -.562 | -.347 | .469 | -.611* | -.466 | -.467 | 1 | -.676* | .638* |
| | Sig. (2-tailed) | .057 | .270 | .124 | .035 | .127 | .125 | | .016 | .026 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |

| | | pH | EC | Nitrate | COD | SS | Ammonia | Phosphate | Temperature | Chloride |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | Pearson Correlation | .585* | .379 | -.828** | .353 | .613* | .374 | -.676* | 1 | -.448 |
| | Sig. (2-tailed) | .046 | .224 | <.001 | .261 | .034 | .231 | .016 | | .144 |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| Chloride | Pearson Correlation | .033 | -.299 | .158 | -.688* | -.327 | -.457 | .638* | -.448 | 1 |
| | Sig. (2-tailed) | .920 | .346 | .624 | .013 | .299 | .135 | .026 | .144 | |
| | N | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| *. Correlation is significant at the 0.05 level (2-tailed). | | | | | | | | | | |
| **. Correlation is significant at the 0.01 level (2-tailed). | | | | | | | | | | |

## 4.4. Pearson correlation analysis of the physicochemical parameters (2023 –2024)

The physicochemical properties' correlation was evaluated to demonstrate the association and magnitude of the linear relationship between two variables. A Pearson's correlation coefficient (r) was computed using the pair of variables for the influent and effluent of the WWTP. As shown in **Table 4.3**, the results showed significant and no significant correlation with each other. The findings show several significant relationships between the indicators of water quality. pH shows a moderate negative correlation with nitrate ($r=-0.623$, $p = 0.031$) and a moderate positive correlation with temperature ($r=0.585$, $p = 0.046$), both significant at the 0.05 level. EC has a strong positive correlation with COD ($r=0.738$, $p = 0.006$) and a very strong positive correlation with ammonia ($r=0.965$, $p < 0.001$), both significant at the 0.01. Nitrate shows a strong negative correlation with temperature ($r=-0.828$, $p < 0.001$) and is significant at the 0.01. COD has a strong positive correlation with ammonia ($r=0.811$, $p = 0.001$), and a moderate negative correlation with both phosphate ($r=-0.611$, $p = 0.035$) and chloride ($r=-0.688$, $p = 0.013$). SS shows a moderate positive correlation with temperature ($r=0.613$, $p = 0.034$) and phosphate shows a moderate negative correlation with temperature ($r=-0.676$, $p = 0.016$) as well as a moderate positive correlation with chloride ($r=0.638$, $p = 0.026$). There are no significant correlations between pH and chloride, EC and chloride. Overall, these findings point to possible interactions in water quality that could be impacted by environmental contamination, with higher ammonia being linked to higher EC and COD and higher temperature being linked to lower nitrate levels. According to Osode and Okoh, (2009) Understanding the nature of the physicochemical characteristics and its species specification on the receiving water body and effluent is made easier by knowing how the variables correlate with one another.

*Table 4.4: Correlations analysis of physicochemical parameters dependent and independent variables.*

| | | pH | Temperature | Electrical conductivity | Ammonia | COD | Nitrate | Suspended solids | Phosphate | Chloride | Chlorine demand |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **pH** | **Pearson correlation** | 1 | 0.173 | 0.737 | 0.679 | 0.312 | -0.567 | -0.649 | -0.139 | -0.059 | -0.926 |
| | **Sg. (2-tailed)** | | 0.827 | 0.263 | 0.321 | 0.688 | 0.433 | 0.351 | 0.861 | 0.941 | 0.074 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Temperature** | **Pearson correlation** | 0.173 | 1 | -0.193 | 0.835 | 0.087 | -0133 | 0.451 | -0.851 | -0.843 | -0.001 |
| | **Sg. (2-tailed)** | 0.827 | | 0.807 | 0.165 | 0.913 | 0.867 | 0.549 | 0.149 | 0.157 | 0.999 |
| | **N** | 4 | 4 | | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Electrical conductivity** | **Pearson correlation** | 0.737 | -0.193 | 1 | 0.211 | -0.344 | 0.082 | -0.365 | -0.141 | -0.084 | -0.937 |
| | **Sg. (2-tailed)** | 0.263 | 0.807 | | 0.789 | 0.656 | 0.918 | 0.635 | 0.859 | 0.916 | 0.063 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Ammonia** | **Pearson correlation** | 0.679 | 0.835 | 0.211 | 1 | 0.320 | -0.483 | -0.068 | -0.660 | -0.610 | -0.480 |

| | | pH | Temperature | Electrical conductivity | Ammonia | COD | Nitrate | Suspended solids | Phosphate | Chloride | Chlorine demand |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Sg. (2-tailed)** | 0.321 | 0.165 | 0.789 | | 0.680 | 0.517 | 0.932 | 0.340 | 0.390 | 0.520 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **COD** | **Pearson correlation** | 0.312 | 0.087 | -0.344 | 0.320 | 1 | -.960 | -0.661 | 0.427 | 0.457 | 0.041 |
| | **Sg. (2-tailed)** | 0.688 | 0.913 | 0.656 | 0.680 | | 0.040 | 0.339 | 0.573 | 0.543 | 0.959 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Nitrate** | **Pearson correlation** | -0.567 | -0.133 | 0.082 | -0.483 | -.960* | 1 | 0.761 | -0.324 | -0.373 | 0.237 |
| | **Sg. (2-tailed)** | 0.433 | 0.867 | 0.918 | 0.517 | 0.040 | | 0.239 | 0.676 | 0.627 | 0.763 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Suspended solids** | **Pearson correlation** | -0.649 | 0.451 | -0.365 | -0.068 | -0.661 | 0.761 | 1 | -0.654 | -0.712 | 0.521 |
| | **Sg. (2-tailed)** | 0.351 | 0.549 | 0.635 | 0.932 | 0.339 | 0<br>.239 | | 0.346 | 0.288 | 0.479 |

| | | pH | Temperature | Electrical conductivity | Ammonia | COD | Nitrate | Suspended solids | Phosphate | Chloride | Chlorine demand |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Phosphate** | **Pearson correlation** | -0.139 | -0.851 | -0.141 | -0.660 | 0.427 | -0.324 | -0.654 | 1 | .977 | 0.172 |
| | **Sg. (2-tailed)** | 0.861 | 0.149 | 0.859 | 0.340 | 0.573 | 0.676 | 0.346 | | 0.003 | 0.828 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Chloride** | **Pearson correlation** | -0.059 | -0.843 | -0.084 | 0.610 | 0.457 | -0.373 | -0.712 | .997 | 1 | 0.100 |
| | **Sg. (2-tailed)** | 0.941 | 0.157 | 0.916 | 0.390 | 0.543 | 0.627 | 0.288 | 0.003 | | 0.900 |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Chlorine demand** | **Pearson correlation** | -0.926 | -0.001 | -0.937 | -0.480 | 0.041 | 0.237 | 0.521 | 0.172 | 0.100 | 1 |
| | **Sg. (2-tailed)** | 0.074 | 0.999 | 0.063 | 0.520 | 0.959 | 0.763 | 0.479 | 0.828 | 0.900 | |
| | **N** | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |

**. Correlation is significant at the 0.05 level (2-tailed).*

| | | pH | Temperature | Electrical conductivity | Ammonia | COD | Nitrate | Suspended solids | Phosphate | Chloride | Chlorine demand |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ***. Correlation is significant at the 0.01 level (2-tailed).* | | | | | | | | | | | |

**Table 4.4** illustrates a strong positive correlation between electrical conductivity (r = 0.737) and pH and ammonia (r = 0.679), although not statistically significant. There were negative correlations between temperature and both phosphate (r = -0.851) and chloride (r = -0.843), a strong positive association between temperature and ammonia (r = 0.835), and a substantial negative correlation between pH and chlorine demand (r

= -0.926, p = 0.074). COD and nitrate showed a statistically significant negative connection (r = -0.960, p = 0.040). The correlation between chlorine demand and specific water quality measures provide information about potential environmental risks to aquatic life and river ecosystems. Although they are not statistically significant, higher concentrations of COD (r = 0.041), nitrate (r = 0.237), suspended particles (r = 0.521), phosphate (r = 0.172), and chloride (r = 0.100) all raise the demand for chlorine. This suggests that when both organic and inorganic pollutants rise in the water, more chlorine is required to disinfect it. On the other hand, ammonia

(r = -0.480), pH (r = -0.926), temperature (r = -0.001), and electrical conductivity (EC, r = -0.937) all have negative correlations with chlorine demand. The strong negative correlations between pH and EC that are not statistically significant indicate that chlorine demand tends to decrease at higher pH levels or greater ionic concentration. This could be the consequence of reduced chlorine reactivity at higher pH values or interference from ions that could compete with chlorine. In these situations, a decreased chlorine need might reduce the production of DBP, but an inadequate chlorine dosage could potentially jeopardize the efficacy of microbial control.

Ecologically, high chlorine demand and elevated pollutants are indicators of poor water quality, which is often caused by municipal wastewater discharges. When excess chlorine is used to satisfy excessive demand, residual chlorine and DBPs may be released into rivers, posing major harm to aquatic biodiversity. Fish gill function, aquatic food chains, and dissolved oxygen levels can all be impacted by these substances (Richardson and Kimura, 2016). Additionally, long-term physiological and behavioral changes caused by aquatic species' continuous exposure to chlorine and its metabolites may pose a danger to the sustainability of aquatic ecosystems (Luan

*et al.,* 2020). These results show important relationships between effluent parameters and offer guidance for controlling chlorine dosage and water quality in treatment facilities. These findings provide guidelines for regulating chlorine dosage and water quality in treatment facilities and highlight significant correlations between effluent metrics. Statistically significant associations between different water quality measures were reported by Hayek *et al*. (2020). In summary, the correlation patterns show that pollution-induced increases in chlorine demand not only complicate water treatment processes but also pose indirect threats to aquatic life and riverine ecosystems.

*Table 4.5: Correlations Analysis between free chlorine, chlorine demand and E. coli (2023 – 2024).*

| | | **Free chlorine** | ***E. coli*** | **Chlorine demand** |
|---|---|---|---|---|
| Free chlorine | Pearson Correlation | 1 | .721** | -1.000** |
| | Sig. (2-tailed) | | .008 | <.001 |
| | N | 12 | 12 | 12 |
| *E. coli* | Pearson Correlation | .721** | 1 | -.721** |
| | Sig. (2-tailed) | .008 | | .008 |
| | N | 12 | 12 | 12 |
| Chlorine demand | Pearson Correlation | -1.000** | -.721** | 1 |
| | Sig. (2-tailed) | <.001 | .008 | |
| | N | 12 | 12 | 12 |

***. Correlation is significant at the 0.01 level (2-tailed).*

## 4.5. Pearson Correlation Analysis between free chlorine, chlorine demand and *E. coli* (2023 – 2024).

As shown on **Table 4.5** there is a correlation between Free chlorine, *E. coli*, and

chlorine demand. The results show a strong positive correlation between free chlorine and *E. coli* (r=0.721, p = 0.008), significant at the 0.01. Free chlorine shows a perfect negative correlation with chlorine demand (r=−1.000, p < 0.001), which is significant at the 0.01. This suggests a straight inverse link between the two variables, with an increase in free chlorine leading to a proportionate drop in chlorine demand. *E. coli* shows a strong negative correlation with chlorine demand (r=−0.721, p = 0.008) and significant at 0.01, this suggests that the demand for chlorine falls as *E. coli* levels rise.

According to the findings, *E. coli* levels are positively connected with free chlorine but negatively with chlorine demand, indicating a direct inverse relationship between the two. These connections demonstrate how chlorine may affect the presence of microorganisms and the consequent need for more chlorine treatment.

*Table 4.6: Regression analysis between dependent and independent variables.*

***Model Summary***

| Model | R | R Square | Adjusted R Square | Std. Error of the Estimate |
|---|---|---|---|---|
| 1 | 1.000[a] | 1.000 | . | . |

*a. Predictors: (Constant), Chloride, EC, nitrate, phosphate, PH, SS, COD, Temperature, Free chlorine, ammonia, E. coli*

***ANOVA[a]***

| Model | | Sum of Squares | Df | Mean Square | F | Sig. |
|---|---|---|---|---|---|---|
| 1 | Regression | .206 | 11 | .019 | . | .[b] |
| | Residual | .000 | 0 | . | | |
| | Total | .206 | 11 | | | |

*a. Dependent Variable: Chlorine demand*

*b. Predictors: (Constant), Chloride, EC, nitrate, phosphate, PH, SS, COD, Temperature, Free chlorine, ammonia, E. coli*

***Coefficients***

| Model | | Unstandardized Coefficients | | Standardized Coefficients | T | Sig. |
|---|---|---|---|---|---|---|
| | | B | Std. Error | Beta | | |
| 1 | (Constant) | .500 | .000 | | . | . |

| | | | | | | |
|---|---|---|---|---|---|---|
| | pH | 6.173E-16 | .000 | .000 | . | . |
| | EC | -5.186E-17 | .000 | .000 | . | . |
| | Nitrate | -7.899E-17 | .000 | .000 | . | . |
| | COD | 1.031E-16 | .000 | .000 | . | . |
| | SS | 1.007E-17 | .000 | .000 | . | . |
| | Ammonia | -4.269E-17 | .000 | .000 | . | . |
| | Phosphate | 8.496E-18 | .000 | .000 | . | . |
| | Temperature | -9.460E-16 | .000 | .000 | . | . |
| | Free chlorine | -1.000 | .000 | -1.000 | . | . |
| | *E. coli* | 2.778E-17 | .000 | .000 | . | . |
| | Chloride | -2.823E-17 | .000 | .000 | . | . |
| *a. Dependent Variable: Chlorine demand* | | | | | | |

## 4.6. Regression analysis between dependent and independent variables

The results on **Table 4.6** indicate a perfect correlation *R* (1.000) between the observed and predicted values for chlorine demand. A perfect fit, in which the residual variance is zero, may be the reason why the estimate's adjusted *R* square and standard error are absent. Regression's sum of squares is 0.206, while residual's sum of squares is zero. This shows that there is no residual error in the model, which means that it accurately forecasts chlorine demand with no inexplicable variance. Due to the zero residual sum of squares, the F-statistic and Significance are not computed. This further demonstrates how well the model fits the data. The coefficient of -1.000 for free chlorine shows a perfect inverse connection with chlorine demand. The coefficients of all other variables are nearly negative, indicating that they have little bearing on the model's ability to anticipate chlorine demand and despite being less significant because of the perfect match, the constant value is 0.500. This model demonstrates that, with a perfect negative correlation, free chlorine is the only meaningful predictor of chlorine demand. Chlorine demand in this model does not seem to be predicted by any of the other predictors.

# CHAPTER 5

# Summary, Conclusion and Recommendations

## 5.1. Summary

This study investigated chlorine's efficacy as a disinfectant in the treatment of municipal wastewater and considering and the influence of inorganic and organic chemicals on chlorine demand. Chlorine is used widely, although it is often consumed by side reactions that produce chloramines and other byproducts that reduce its availability for microbial inactivation. The study examines how chlorine and wastewater components interact and delves deeper into the dynamics of chlorine demand in a wastewater treatment plant (WWTP).

Physicochemical and bacteriological analyses were performed seasonally (summer, autumn, winter, and spring) on influent and effluent samples. pH, temperature, electrical conductivity (EC), ammonia, nitrate, phosphate, chloride, suspended solids (SS), chemical oxygen demand (COD), and chlorine residual were among the parameters that were measured. Chlorine demand was only analyzed for effluent samples because there was no chlorine dosing at the influent stage. Seasonal data showed that the demand for chlorine and residual chlorine were inversely correlated, with demand increasing in the winter and residual chlorine peaking in the summer.

*E. Coli* analysis revealed a partial decrease in effluent throughout all seasons, along with noticeably high microbiological burdens in influent samples (>100,000 MPN/100 mL). Correlation and regression analyses were conducted using SPSS revealing statistically significant relationships between chlorine demand and several water quality parameters. There was a negative correlation between chlorine demand and ammonia, EC, temperature, and pH, but a positive correlation with COD, SS, nitrate, phosphate, and chloride. Chlorine demand and these parameters are highly predictable, as indicated by the perfect regression correlation (R = 1.000) between the observed and anticipated chlorine demand values.

Parameters such as temperature, EC, pH, SS, chloride, and free chlorine were all

within acceptable WHO (2007) limits, while *E. coli*, nitrate, ammonia, phosphate, and COD were all above the recommended thresholds. The findings highlight the importance of both organic and inorganic pollutants in increasing chlorine demand, decreasing disinfection effectiveness, and causing environmental impacts such aquatic toxicity and eutrophication. The study concludes that it is necessary to have better pretreatment and nutrient removal techniques to increase chlorine efficiency, mitigate ecological harm, and save operating expenses. Public health and the receiving aquatic environment may be at risk due to the current state of the WWTP.

## 5.2. Conclusions

This study investigated the reaction and effects of inorganic and organic compounds on chlorine demand in wastewater treatment plants (WWTP). The collected data, supported by literature, revealed that high chlorine demand and reduction of the availability of residual chlorine required for microbiological inactivation in WWTP is influenced by high levels of organic and inorganic compounds in water. Seasonal fluctuations also affect disinfection efficiency; residual chlorine levels are inversely correlated with chlorine demand, which peaks in the winter and falls in the summer. High levels of ammonia, COD, phosphate, and suspended particles in the effluent greatly increased the demand for chlorine, leading to insufficient disinfection, as seen by consistently high *E. coli* levels throughout all seasons. The study emphasizes how organic and inorganic chemicals affect wastewater treatment plant's need for chlorine. The demand for chlorine is greatly increased by inorganic substances such as nitrates and ammonia that react with it to produce chloramines or other byproducts.

There was a negative link between pH and electrical conductivity (EC), statistical analysis verified a positive correlation between chlorine demand and parameters such as COD, suspended solids, and nitrate. Water parameters like ammonia, phosphate, nitrate, COD, and *E. coli* exceeded WHO (2007) standards, suggesting reduced treatment performance, even if free chlorine, temperature, pH, and EC generally stayed within permissible limits. In addition to raising operating expenses because of excessive chlorine consumption, these inefficiencies produce hazardous disinfection by-products (DBPs), which endanger the environment by causing aquatic toxicity and

eutrophication. Overall, the results show that better treatment methods are required to increase chlorine efficiency and safeguard the environment and human health.

## 5.3. Recommendations

The following recommendations must be examined in future studies due to the study's narrow scope and the setting of the future:

- Reduce ammonia, phosphate, and organic load prior to chlorination by introducing advanced primary or secondary treatment stages (such as nitrification or phosphorus removal).
- Adapt chlorine dosage rates to seasonal demand trends to maintain sufficient residual levels even during periods of high demand, such as winter season.
- Instead of using chlorine, consider UV or ozone disinfection to lower DBPs and increase microbiological death rates.
- Introduce chloramination under regulated conditions, if longer-lasting disinfection is required though this may still result in by-products.
- Use biological nutrient removal (BNR) approaches to efficiently control phosphate and nitrate levels and avoid eutrophication in receiving waters.
- Monitor effluent for trihalomethanes (THMs) and other DBPs on a regular basis.
- Regular monitoring of the physicochemical properties of WWTP effluent is necessary to protect human health from exposure and the ecological well-being of receiving waterbodies
- Assess the receiving waterbody ecotoxicologically to monitor long-term environmental effects.

- Organize activities in accordance with local and WHO regulations on effluent quality.
- Enhance the training of operators in process control and chlorine management.
- The fundamental chemical, biological, and/or physical characteristics linked to the variations in parameter values that influence the diffusion and reaction of chlorine in wastewater effluent.

# Appendices

## Appendix A: Consent Form

UNISA university of south africa

**Consent Form**

**STUDENTS INFORMATION**

Names: Florence Sebati
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Date: 04/05/2022

**TITLE OF RESEARCH PROJECT:**

The reaction and effects of inorganic and organic compounds on chlorine demand in wastewater treatment plant

To: SEWATREAT

**NATURE AND PURPOSE OF THE STUDY**

I am Florence Sebati an MSc student at the University of South Africa (UNISA), College of Agriculture and Environmental Sciences, Department of Environmental Science. I wish to request your permission to undertake a master's research project at Hibron Mall WWTP which involves site visit, provision of process information and sample collection. The student has been registered as from 10 January 2022 and would like to be granted permission to use SEWATREAT as the study area for research proposal and dissertation between 2022 and 2023 academic years. This study will require sampling for results analysis; thus, the above student would like to be granted approval for site sampling as from January 2023 for the period of the study. We will be sampling at allocated wastewater treatment plant at the inlet works raw water and final effluent. Water samples will be collected once a month for a period of one (1) year. The physico-chemical parameters and bacteriological assessment will be measured on site. We will appreciate if we can be allowed to conduct this study as it is critical to monitor organic and inorganic compounds in treatment works as they create high chlorine demand when reacting in water. According to the literature it is wasteful to satisfy chlorine demand because more chlorine is consumed for disinfection than is required. Therefore the study will help SEWATREAT to identify the sources of high chlorine demand and minimize the cost of disinfection.

## Appendix B: Ethics Clearence Letter

UNISA university of south africa

**UNISA-CAES HEALTH RESEARCH ETHICS COMMITTEE**

Date: 06/06/2023

Dear Ms Sebati

NHREC Registration # : REC-170616-051
REC Reference # : 2023/CAES_HREC/063
Name : Ms NF Sebati
Student #: 61938882

**Decision: Ethics Approval from 01/06/2023 to 31/05/2026**

---

**Researcher(s):** Ms NF Sebati
61938882@mydfe.unisa.ac.za; 063-873-2969

**Supervisor (s):** Dr T Mhlongo
eshongtn@unisa.ac.za; 011-471-2655

**Working title of research:**

The reaction and effects of inorganic and organic compounds on chlorine demand in wastewater treatment plant

**Qualification:** MSc Environmental Management

---

Thank you for the application for research ethics clearance by the Unisa-CAES Health Research Ethics Committee for the above mentioned research. Ethics approval is granted for three years, **subject to further clarification and submission of yearly progress reports. Failure to submit the progress report will lead to withdrawal of the ethics clearance until the report has been submitted.**

**Due date for progress report: 31 May 2024**

The progress report is available on the college ethics webpage: https://www.unisa.ac.za/sites/corporate/default/Colleges/Agriculture-&-Environmental-Sciences/Research/Research-Ethics

*Please note the points below for further action:*

1. Please submit the permission letter from the Ekurhuleni Watercare Company for use of the laboratory facility.

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## Appendix C: First page of Turnitin Report

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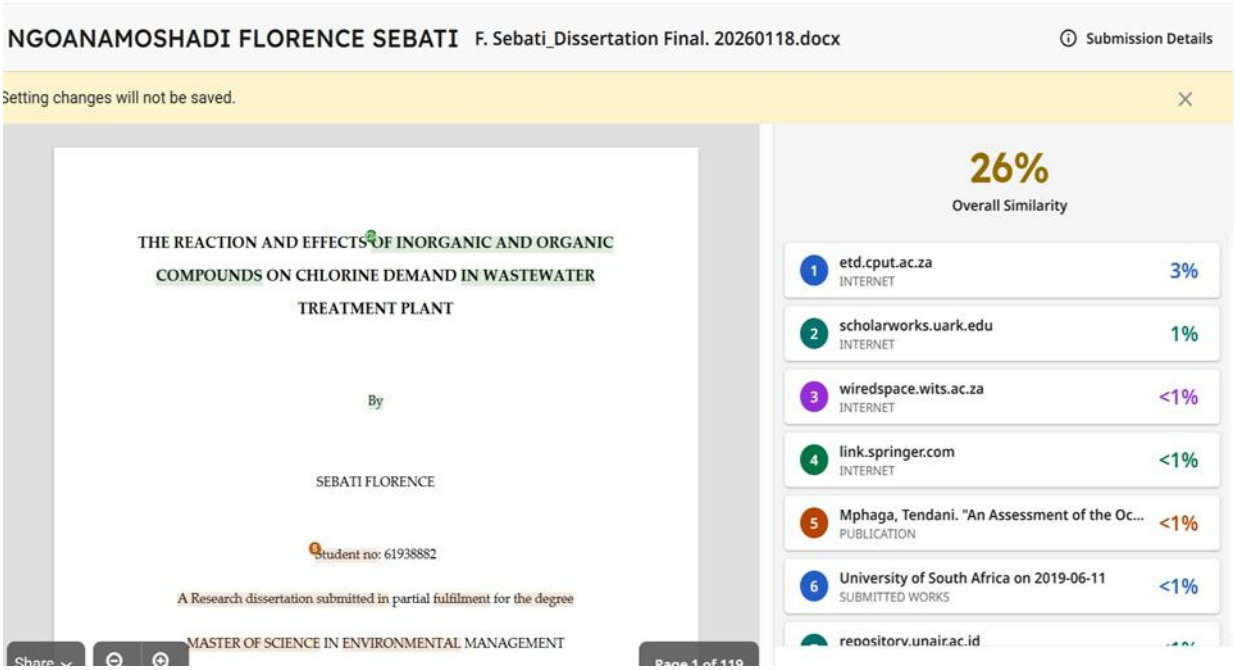

## Appendix E: Motivation for Turnitin Similarity Report

**Motivation for Turnitin Similarity Report**

**To:** Research office

**From:** Dr Thandazile N. Mhlongo

**Date:** 13 January 2026

**Re: Ms NF Sebati 61938882_MSc Environmental Management Turnitin score**

---

The Turnitin similarity report for this dissertation indicates a 26% similarity score. Upon review, it has been determined that the similarity is primarily due to non-substantive elements of the document, including:

- The cover page
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Considering this, the Turnitin similarity score does not compromise the originality or academic integrity of Ms Sebati's dissertation.

Regards
Yours Sincerely

**Dr Thandazile Ntombie Mhlongo**
t: + 27 21 959 6995 e: mhlongot@cput.ac.za |

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