Impact of Chlorine and Wastewater Contact Time, Chlorine Residual and Mixing on Microorganism inactivation

AHUIWI EMMANUEL NETSHIDAULU

Degree of Master of Science in Civil Engineering (Water)
By
Research Report and Coursework

Research report submitted to the Faculty of Engineering and Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Civil Engineering (Water)

Johannesburg, 2015

DECLARATION

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

(Signature of candidate)

--------------------- day of -----------------------2015

DEDICATION

For my daughter Nkateko and my Son Tshifhumulo

ABSTRACT

This study investigates the effectiveness of chlorine as the disinfectant employed in the wastewater treatment plants operated by Lepelle Northern Water and generally within most municipal wastewater treatment works. The literature review reveals that much of the chlorine demand is ultimately wasted, since reactions competing with the disinfection process results in the formation of chloramines and other by-products not related to chlorine's primary purpose of inactivating micro-organisms in the water. The investigation focused on the following aspects:

- The impact of chlorine and wastewater contact time and chlorine residual concentration on micro-organism inactivation while reducing chlorine dose and aiming not to meet chlorine demand.
- The impact of mixing on the effective disinfection of effluent at the point of chlorination.

Literature shows that although various alternatives to chlorine are available, chlorine remains user-friendly and the cost-effective option for the disinfection of wastewater.
The formation of chlorine residual in sewage effluent for inactivation of bacteria and prevention of regrowth is not as necessary as it is in drinking water systems where the chlorine residual has to be maintained throughout the distribution system. It is therefore a wasteful exercise to satisfy the chlorine demand in wastewater (sewage) effluent discharged into water courses. It is also worth noting that the only purpose of chlorine in wastewater effluent disinfection is to inactivate microorganisms. There is no need to prevent the recontamination of water since the effluent in most municipal sewage treatment plants are immediately discharged into a water course and the chlorine residual in the effluent must not be detected since it is toxic to aquatic life. This study therefore examines the potential disinfection effectiveness of chlorine without meeting chlorine demand or reaching breakpoint chlorination and mixing at the point of chlorination.

The results obtained from a full-scale wastewater treatment plant effluent quality monitoring programme were used as baseline information and reference for this study.

By comparing the observed micro-organism (that is; E. coli) inactivation in the full-scale chlorine systems with E. coli inactivation determined under laboratory conditions, it is conclusive in the literature

that chlorination in practice appears to be much less effective than could be expected under laboratory conditions. In the literature, one study shows that suboptimal hydraulics of full-scale systems are known to reduce the efficacy of inactivation in practice. However, this study indicates that when mixing is applied at the point of chlorination, significant and comparable inactivation can be achieved at a full-scale and at a laboratory scale. This was confirmed in another study which reported rapid initial E. coli inactivation upon contact with free chlorine. Therefore, when a specific optimal mixing regime is determined and applied at the point of chlorination, effective E. coli inactivation in the water is achieved irrespective of the kinetics applicable either at a laboratory scale or in a full-scale system.

This study examines the potential disinfection effectiveness of chlorine without meeting chlorine demand or reaching breakpoint chlorination and mixing at the point of chlorination. The results obtained shows that E. coli inactivation occur at two rates, an initial rapid kill followed by a slower kill. For each applied chlorine dose, the highest inactivation rate was obtained during the first one minute of contact time, which could be due to the presence of free chlorine residual that had not yet reacted with chlorine demanding substances (organics and chemicals). The subsequent slower kill can possibly be attributed to the formation of less potent combined chlorine residual as a result of reactions between free chlorine residual and chlorine demanding substances (mainly NH_3).

This study revealed that rapid mixing of chlorine with wastewater may achieve the required degree of disinfection by using less chlorine, and this will result in significant savings in chlorine dosing. This proposition was confirmed in this study by tests conducted in a full-scale investigation, where the chlorine dosage required to inactivate E. coli at the Burgersfort WWTW effluent was reduced by 50% from the mode of 6.43 mg/l before mixing to the mode of 3.0 mg/l after mixing.

For effective chlorination, a disinfection system must be designed within wastewater treatment works for the wastewater to flow turbulently throughout a chlorine contact chamber and/or dosing point in order to achieve complete mixing within 1 minute of contact time. The mixing allows the maximum dispersal of the free chlorine in the wastewater and contact between chlorine and the microorganisms in the effluent. This ensures effective inactivation before the free chlorine reacts with other impurities present in wastewater that demand chlorine.

ACKNOWLEDGEMENTS

I would like to express my deep gratitude to my supervisor, Prof. A.A Ilemobade for his guidance, supervision, commitment, encouragement and his input over the course of this research. Thank you for the opportunities you gave me to progress in my academic studies.

My heartfelt thanks to Lepelle Northern Water for allowing me to conduct this study using the company resources.

I am also grateful to my **family, friends and colleagues** for their encouragement, understanding and support through this journey.

Most of all, I give glory to my Lord and Saviour **Jesus Christ** for abundant Grace.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

LIST OF SYMBOLS AND ABBREVIATIONS

COD	Chemical Oxygen Demand
Cl_2	Chlorine
DWS	Department of Water and Sanitation
DBPs	Disinfection by-products
E. coli	Escherichia Coli
HTH	Calcium Hypochlorite
HRT	Hydraulic Retention Time
mg/l	milligram per litre
NWA	National Water Act
WSAt	Water Services Act
pH	Power of hydrogen
UV	Ultraviolet absorbance
WWTWs	Wastewater Treatment Works
WSA	Water Services Authority
WSP	Water Services Provider
SANAS	South African National Accreditation Services
STD	Standard

DEFINITION OF CONCEPTS

Chlorination:	The application of chlorine or chlorine compounds to water or wastewater, usually for the purpose of pathogen reduction. In some circumstances, chlorination may also provide chemical oxidation and odour control.
Disinfection:	A process that destroys, inactivates or removes micro-organisms.
E. coli:	*Escherichia coli*. A bacterium found in the gut of warm-blooded animals that indicates faecal contamination.
Effluent:	Final water of wastewater treatment works after treatment processes.
Influent:	Raw water into wastewater treatment works before treatment processes.
Pathogens:	Organisms capable of causing disease. In untreated wastewater, the key potential pathogens include bacteria, viruses, protozoans and helminths.
Residual	A chemical used or produced during the disinfection process that is present at the completion of that process.

CHAPTER 1

1 INTRODUCTION AND BACKGROUND OF THE STUDY

1.1 INTRODUCTION

Most municipal wastewater treatment plants use physicochemical processes to treat domestic and combined domestic and industrial wastewater. These processes include screening, grit removal, addition of ferric chloride and/or alum, as well as a polyelectrolyte to improve solids coagulation, flocculation and settling and effluent disinfection prior to discharge into the receiving streams or rivers (Gehr *et al.*, 2003).

Disinfection of water implies the inactivation, deactivation or killing of pathogenic microorganisms and is used to achieve the standard for E. coli or faecal coliforms as stipulated by the South African general and special limits for treated wastewater effluent (DWAF, 1996). Chlorine has been the dominant disinfectant for wastewater and is still widely (Winward *et al.*, 2008; Amiri *et al.*, 2010; Rauen *et al.*, 2012; Li *et al.*, 2013). It offers a reliable reduction of pathogenic microorganisms at reasonable operating costs. There are, however, various methods that can be used for disinfection. These include physical processes (e.g. ultraviolet radiation) and chemical processes (e.g. Chlorine dioxide, Bromine, and Ozone) (Metcalf & Eddy, 1991; Lim *et al.*, 2010).

Despite the diversity of disinfectants that can be applied to water and wastewater disinfection, chlorination is by far the most common method aslo used by South African municipal water authorities for disinfecting wastewater effluent prior to its discharge into receiving water bodies (Silva, Daniel & Brunin, 2010).

According to Momba (2006), the current wastewater disinfection practice and guideline in terms of chlorine residuals were found not to be sufficient for the inactivation of the target pathogens since high pathogen Count could still be detected in the final effluent tested. Wastewater-related microorganisms demonstrate different sensitivities to chlorination and these sensitivities are dependent on the species of chlorine present and the dose of chlorine applied (Li *et al.*, 2013).

Various literature sources mention that the following factors have to be considered when applying disinfection agents (Metcalf & Eddy, 1991; AWWA, 2002; White, 1999; Charrois & Hrudey, 2007): contact time, disinfectant concentration and type, number and age of organisms, type of organism, constituents in the effluent, temperature, chlorine demand and mixing.

One of the most important variables in the disinfection process is the contact time between the disinfectant and the effluent. In general, the longer the contact time for a given concentration, the more efficient the disinfection (Ibanez *et al.*, 2008). The product of dosing concentration and contact time (Ct) is commonly used to determine the effect of a particular disinfectant against a certain microorganism under specified conditions (Lenntech, 2012).

Depending on the disinfectant type, within limits, disinfection effectiveness is related to concentration (Metcalf & Eddy, 1991). The time required to deactivate a particular microorganism decreases when the applied disinfectant concentration (mg/L) is increased (Lenntech, 2012). To disinfect bacteria, not more than 0.4 mg/L of chlorine may be typically required (Pasco *et al.*, 1994; Pretorius, 1999; Momba & Makala, 2004). The concentrations of chlorine added to the effluent at wastewater treatment plants are usually higher because of the chlorine demand of the water.

In wastewater treatment systems, the concentration of organisms is seldom a major consideration. However, the larger the organism concentration, the longer the time required for effective disinfection. The disinfection effect of a particular disinfectant also depends on the age of the microorganism. Young bacteria are easier to disinfect than older bacteria. When bacteria grow older, they develop a polysaccharide shell over their cell wall, which makes them more resistant to disinfection (Lennetech, 2012).

The effectiveness of various disinfectants is influenced by the nature and condition of the microorganisms present in the effluent. For example, certain spores are extremely resistant to many of the chemical disinfectants normally used for disinfection (Li et al., 2011). E.coli bacteria, for example, are more resistant to disinfectants than other bacteria and are therefore used as indicator organisms. Several viruses are even more resistant than E. coli. The absence of E. coli bacteria does not mean that the water is safe. Protozoan parasites like Cryptosporidium and Giardia are very resistant to chlorine (Lenntech, 2012).

The constituents in the effluent will impact on disinfection. For example, turbidity will reduce the effectiveness of disinfectants by protecting entrapped bacteria. Chemical substances in the water, e.g. iron, manganese, hydrogen sulphide and nitrates, often react with disinfectants, thereby limiting disinfection potency (Lenntech, 2012).

The temperature of the effluent also influences the effect of disinfection. High temperatures (above room temperature) usually increase the speed of certain chemical reactions in the effluent and thus reduce disinfection (Lenntech, 2012). These high temperatures can also decrease disinfection due to the volatility of the disinfectant.

Since chlorine is a very reactive chemical, it also reacts with other substances present in the water, such as organic and inorganic materials that may include reduced metals, sulphides, bromine ions, organic and inorganic nitrogenous compounds (Metcalf & Eddy, 1991). These compounds create a chlorine demand and free chlorine is only available once the demand by these compounds has been satisfied. Satisfying the chlorine demand by other substances apart from disinfecting microorganisms is called breakpoint chlorination and is wasteful because more chlorine is consumed than is required for disinfection alone (Pretorius, 1999). A consequence of this is that the wastewater treatment process increases the cost of chlorine required for disinfection. Unfortunately, the total chlorine demand currently determines chlorine dosage in most water treatment processes. Consequently, to adequately disinfect wastewater, higher disinfectant concentrations are employed to kill pathogenic microorganisms.

Longly (1978) evaluated turbulence factors in chlorine disinfection of wastewater in addition to the above-mentioned factors. He found that the inactivation of microorganisms achieved during disinfection may not always be adequately predicted by the above-mentioned factors (especially chlorine residual and contact time) but could be predicted by the mixing of chlorine with the incoming wastewater. To date, the impact of mixing on chlorine disinfection has not been directly researched and/or applied. Longly (1978) indicates that before the chlorine is thoroughly mixed with the mass of incoming wastewater, reactions competing with the disinfection process results in the formation of chloramines, other by-products and the rapid depletion of free chlorine.

Several reports (DWA 2011; 2012) describe certain critical issues with potable water and wastewater chlorination that deserve mention at this juncture. For example:

- Poor disinfection has been observed at certain plants despite sufficient chlorine in the water. The problem is likely due to the need for upstream changes to process technology and the optimisation of other plant processes.

- The South African Department of Water and Sanitation (DWS) general and special permits for discharge wastewater effluent into water courses respectively call for a 0.1 mg/l and non-detection of chlorine residual (DWAF, 1996).

The residual chlorine requirements are necessary due to residual chlorine's toxicity to aquatic life and the effluents' carcinogenic and toxic compounds arising from chlorine disinfection (Acher *et al.*, 1993). Thus, due to the residual chlorine requirement and the high cost of chlorination based on high chlorine demand (most of which is wasted), there is a growing interest in the application of disinfectants other than chlorine (e.g. chlorine dioxide and ozone) for wastewater effluent disinfection (Warriner *et al*., 1985). Warriner *et al.*, (1985) found that among the chemical disinfectants tested, chlorine was the dominant agent for either water or wastewater disinfection and is usually the economic choice for disinfection of wastewater effluent, especially if de-chlorination is not required. However, since the compliance requirement for free chlorine residual in the effluent for discharging should be <0.1 mg/l (NWA, 1998 & DWAF 1996), there is a need to look at optimising chlorine's effectiveness and its economics.

This study is therefore motivated to address the following issues:

i. Since it is important to look at options to reduce chlorine demand and redirect the chlorine dose to its primary aim of microorganism inactivation without the total chlorine demand being met, this study evaluates the impact of contact time (Ct) and chlorine residual concentration on wastewater treatment (which addresses the effectiveness of chlorine as a disinfectant for wastewater effluent), as well as the correlation between chlorine demand and certain water quality parameters (that is, temperature, COD, ammonia nitrogen and suspended solids/turbidity). It is anticipated that this investigation would assist relevant authorities at wastewater treatment plants to reduce the cost of chlorine dosage while enhancing disinfection efficiency.

   If the above is achieved and the free chlorine residual in the effluent is reduced to zero, this will address the problem faced by most wastewater treatment plants producing above zero free chlorine residual in the effluent discharged into water resource. Hence, this solution will be ecologically beneficial for.

ii. The effectiveness of mixing at the point of chlorination. This study will aim to develop turbulence factors in wastewater effluent disinfection in order to reduce the contact time required between chlorine and the effluent, and the need to meet chlorine demand.

iii. The study investigates reducing the cost of chlorine disinfection based on the above bullet-points. The motivation of this and the above bullet-point is to achieve optimum disinfection with a lower chlorine dose compared to the current chlorine dose practice and consequently, reduce the cost of chlorine disinfection. This will reduce the cost of wastewater treatment operation and also minimise the need to de-chlorinate high chlorine residual in the effluent before discharge.

1.2 SUMMARY OF THE PROBLEM

Chlorine dose demand during disinfection of wastewater effluent is unrealistically high because the chlorine reacts with organic and inorganic materials that the chlorination is not primarily aimed at. Part of what is needed is a better understanding or acknowledgement of chemical reactions that occur simultaneously during chlorination (Amiri, *et al*., 2010). The current practice of disinfection therefore warrants the need to satisfy the chlorine demand before disinfection can proceed. Gehr *et al*., (2003) affirms that if there is little organic matter in the effluent, the disinfection reaction will be faster than is currently the norm.

As mentioned earlier, chlorine dosages lower than 0.4 mg/l could be sufficient to disinfect and achieve up to 99% microorganism inactivation (Pasco *et al*., 1994; Amiri *et al*., 2010; Metcalf & Eddy, 1991) and the maximum hydraulic retention time (HRT) to achieve complete inactivation of E. coli is 2.5 minutes, corresponding to the initial E. coli concentration of 108 Count/100 ml (Nanayakkara *et al*., 2012). Therefore, this study asks the following questions:

- ***Can optimum microorganism inactivation take place during wastewater disinfection without the need to first meet the total chlorine demand?***
- ***Consequent to the above, can the wastewater effluent discharge standard for E. coli as the definitive preferred indicator of faecal pollution microorganisms be achieved with chlorine dosage concentrations lower than what is currently required to produce 0 mg/l of free residual chlorine?***

1.3 RESEARCH AIM AND OBJECTIVES

The aim of this research is to evaluate and optimize the effectiveness of chlorine as a disinfectant for wastewater treatment effluent discharged into water bodies.

Specific Objectives

i. To empirically evaluate the impact of chlorine and wastewater contact time (Ct) and chlorine residual concentration on microorganism inactivation, while reducing chlorine dose and aiming not to meet chlorine demand.

ii. To empirically evaluate the impact of mixing on effective disinfection at the point of chlorination.

1.4 SUMMARY OF RESEARCH METHODS AND MATERIALS

This research project is based on primary data collected at the Burgersfort wastewater treatment works operated by Lepelle Northern Water.

Literature review is presented to understand mixing during disinfection dosing, and the effective inactivation of microorganisms using disinfectants.

Full-scale investigations

The Burgersfort wastewater treatment plant operated by Lepelle Northern Water Board was employed as the full-scale plant during the study period. The Laboratory facility of Lepelle Northern Water was used to conduct the experiments and the analyses of samples. The bench scale (discussed) chlorine demand test results were compared with chlorine demand results obtained at the Burgersfort wastewater treatment plant. The same was undertaken for bacteriological quality of the wastewater effluent discharged.

Bench scale investigations

The methodology applied for bench scale investigations is as follows:

Chlorine solution preparation and analysis

The chlorine solution used in the bench scale experiments was Calcium Hypochlorite (HTH) and/or chlorine gas diluted with distilled water to obtain a stock solution of approximately 600-800 mg/l free chlorine concentration, measured using a an HACH pocket colorimeter.

Chlorine demand tests

The following stapes were undertaken in order to determine chlorine demand:

- Starch, 0.025N sodium thiosulphate and HTH solutions were prepared for this test.
- Volumetric flasks were filled with 100ml of the primary effluent (i.e. un-chlorinated wastewater).
- The determined volume (e.g. 0.5ml, 1.0ml, 1.5ml etc.) of standardised HTH solution were added to each flask and the intervals between additions (e.g. 1 minute) were noted.
- Immediately after adding the HTH solutions to each flask, the cap was screwed on and the flask shaken. Thereafter, the flask was kept in a dark place for 30 minutes.
- After 30 minutes, each flask was shaken again and a 10 ml sample was withdrawn and free chlorine concentration measured using a HACH pocket colorimeter.
- The readings obtained were plotted and measured the breakpoint chlorination determined from the graph.

Disinfection experiments using chlorine

Five litre dark non-transparent glass bottles were filled with primary effluent and chlorinated by adding liquid chlorine. These samples were used to empirically evaluate the impact of chlorine and wastewater contact time (Ct) and chlorine residual concentration on microorganism inactivation, while reducing chlorine dose and aiming not to meet chlorine demand.

E. coli count was measured because E. coli is a well-known indicator organism, it is faecal specific and can be analysed quickly, efficiently and cost effectively. Furthermore, E. coli is more resilient to chlorination than other pathogens excreted in human faeces and occurs more abundantly.

To empirically evaluate the impact of mixing on effective disinfection at the point of chlorination, chlorine concentrations were dosed into each of three 5-litre dark glass bottles. Variable mixing rates were applied to each bottle to evaluate the impact of mixing.

1.5 DELINEATION AND LIMITATIONS OF THE STUDY

This study is confined to the use of chlorine as a disinfectant for wastewater treatment plant effluent. Some major limitations include:

- The study only evaluates the effectiveness of chlorine as a disinfectant for wastewater and not other alternative disinfectants.
- The study does not assess the impact of the efficiency of treatment units upstream of the disinfection process unit, but do evaluates the inactivation of microorganisms irrespective of the quality of wastewater in the disinfection unit.
- The detailed kinetics of chlorine's different reactions with inorganic and organic materials in solution, chlorine's interaction with microorganisms, and chlorine's decomposition in the effluent do not form part of this study. Hence, a disinfection kinetic model is not developed.
- This study focuses on the indicator aerobic bacteria (i.e. E. coli) prescribed in the South African General and Special standards (DWAF, 1996) which shows a relative low resistance to chlorine. In other words, microorganisms that cannot be inactivated by chlorine due to their greater resistant to chlorine disinfection are not assessed in this study.
- The effects of suspended solids, chorine dose concentration and contact time are studied in relation to mixing or turbulence at the point of disinfection.

- The effects of temperature and pH on the inactivation kinetics of bacteria by chlorine, as well as the diffusion rate of chlorine under different conditions are not studied as part of this research.

Therefore, this work only assessed effect of the suspended solids, chorine dose concentrations and contact time on the effect of applying mixing or turbulence at the point of disinfection. Neumann et al., (2007) in their study indicated that bacteria inactivation is quantified as a function of disinfectant exposure (i.e. Ct). Other factors that also have an impact on the effectiveness of disinfection where not verified. No effort was made to distinguish between the two free chlorine species present (hypochlorite and hypochlorous acid) or the formation of chloramines.

In this study, experiments were performed in a limited number of conditions, and thus the effects of temperature and pH on the inactivation kinetics of bacteria with chlorine remain to be fully characterised, as well as the diffusion rate of chlorine under different conditions.

1.6 LAYOUT OF THE STUDY

The paragraphs below and Figure 1.1 propose the layout of this research report.

CHAPTER 1: Introduction

This chapter presents the context of the study and formulates the problem statement, research objectives, and summary of methods and materials.

CHAPTER 2: Literature Review

This chapter presents the literature review carried out during this study and provides a theoretical background to wastewater disinfection and chlorination.

CHAPTER 3: Materials and Methodology

This chapter discusses in detail the materials and methods employed to address this study's objectives.

CHAPTER 4: ***Results and Discussion***

This chapter highlights the findings of the study and relates these to the research objectives outlined in Chapter 1.

CHAPTER 5: ***Conclusion***

Highlights and conclusions derived from the research are discussed. This final chapter makes recommendations for further improvement.

CHAPTER 2

2 LITERATURE REVIEW

2.1 INTRODUCTION

This literature review offers a comprehensive look at chlorine disinfection of water, wastewater treatment works and its effectiveness.

Wastewater is the source of many human enteric pathogens and often associated with diseases contracted through swimming in natural waters. Adequate wastewater treatment prior to effluent discharge plays a critical role in minimizing public health risks (Srinivasan, 2011). Tyrrell (1995) indicated that during the past decade, epidemiological data in the United States have shown a dramatic increase in outbreaks of enteric viral diseases transmitted by recreational water and shellfish. This increase is, at least partially, a result of the inadequacy of chlorination, as practiced by most US wastewater treatment facilities to effectively inactivate many viral agents.

The impact of untreated/partially treated wastewater has raised several health and safety concerns. As both industry and populations continue to increase, there is an increase in wastewater generation in urban areas and a great decrease in freshwater availability. Every year, hundreds of billions of litres of partially treated sewage flows into rivers and lakes for one reason or another (DWA, 2009, Li & Zhang, 2013). Most wastewater treatment plants do not fully treat their wastewater. Partially treated or untreated sewage contains a wide array of pathogens that pose a health risk. Partially treated sewage discharged into the environment can percolate into ground water, contaminating drinking water wells with pathogens. It can also damage the receiving stream's ability to support healthy, living communities of aquatic organisms. (Li & Zhang, 2013, Adewumi *et al*., 2010).

Golder Associates Africa and Zitholele Consulting (2006a) points out that the regulatory framework for wastewater treatment works in South Africa points out two critical factors that force a need for high quality discharge from wastewater treatment works (WWTWs):

- the Country is approaching maximum economic exploitation of available surface and groundwater resources and high quality discharges are required to protect the limited water resources; and

- the Country continues to face deterioration in the quality of the surface water resources due to the discharge of poorly treated wastewater.

As result, the quality of discharges from wastewater treatment plants has become a matter of national importance and priority (Adewumi, Ilemobade & van Zyl, 2012). Both the establishment and operation of a wastewater treatment plant and the discharge of treated wastewater are subject to laws and regulations implemented by the Department of Water and Sanitation (DWS). Community concerns about environmental pollution resulting from the quality of wastewater disposed into sensitive environments has led to pressures on the water industry to treat wastewater at a higher level before discharging into receiving rivers or streams (Adewumi, Ilemobade & van Zyl, 2010).

Recently, the fate of antibiotics, their presence in wastewater and their potential toxic effects have gained the attention of environmental researchers throughout the world (Li & Zhang, 2013; Xu *et al*., 2011). In South Africa, the Government (Department of Water and Sanitation) has become more and more concerned about potential pollution due to municipal wastewater treatment works that are in a desperate state. The Green Drop incentive regulation initiative was introduce to ensure that an environment is created within the water sector where wastewater is once again prioritised by water service authorities. However, the efforts of water service authorities and water service providers to ensure compliance with the effluent discharge standard for E. coli has led to an increase in the cost of disinfection treatment and non-compliance to standards of residual chlorine discharged into the water course. This research was subsequently initiated to find an effective method of disinfection and to enhance the disinfection process via disinfection process optimisation without compromising disinfection and creating by-products that result in non-compliance when it comes to the discharged effluent.

2.2 WASTEWATER EFFLUENT REGULATORY FRAMEWORK

Water Services Legislation: Prior to the Water Act 54 of 1956, the Union Health Act of 1919 required land disposal of treated wastewater and prohibited local authorities from discharging wastewater into water resources without special permits. In contrast to this, the Water Act 54 of 1956 made it obligatory to return treated wastewater to the source river or dam. The Water Act (1956) also stipulated the required standards that must be met when treated wastewater is discharged into the environment. The standards were published in order to manage water quality problems such as salinisation and eutrophication. The promulgation of regulations that prescribed General and Special Standards (1962) and the Special Standard for Phosphate (1980) in terms of this Act was aimed at combating increasing water quality problems by stipulating stricter requirements for discharge quality (Government Gazette, 1984).

The above regulation superseded by the National Water Act No. 36 of 1998 (NWA). The NWA combines receiving water quality objectives and pollution prevention approaches to produce discharge standards specific to local catchments. This approach is aimed at ensuring the long-term sustainable use of limited water resources. This approach combines source-directed and resource-directed measures to ensure that the receiving water environment is “fit-for-use” by all legitimate water users.

The source-directed regulatory measures focus on water resource impacts from both point and diffuse sources. These measures are aimed at managing and controlling the generation of waste at source. The resource-directed measures focus on the receiving water body. The aim of these measures is to set clear objectives for a water resource to attain a certain level of protection and to satisfy the water quality requirements of legitimate water users. These measures require that water resources should be grouped into different classes of protection, with associated water resource quality targets.

Section 21 of the NWA allows for the discharge of water containing waste (wastewater) into a water resource as a licensed water use. A person or institution may only discharge wastewater to a water resource if that discharge is authorised (which could either be by a license, a general authorisation or a continuation of a pre-existing lawful use). The wastewater must be treated so that its quality reliably complies with the standards contained in the relevant authorisation. These discharge standards are determined based on the local and regional water resource quality objectives and reflect both the precautionary approach and local catchments approach.

Section 26(1) (h) of the NWA further states that the DWS Minister can regulate the waste standards pertaining to the waste that may be discharged into a water resource. Draft regulations have been published that cater for three different discharge standards, covering existing discharges, new discharges and a future stage applicable to all discharges. At present, the discharge standards specified in the General Authorisation, No. 339 of March 2004, are used as a guideline to set wastewater discharge standards in the absence of resource-derived water quality objectives.

While the establishment and operation of a wastewater treatment plant and associated wastewater discharges are regulated in terms of the National Water Act, the provision of sanitation services, which includes sewage and wastewater services (e.g. Bulk sewer pipelines for collection, monitoring influent and effluent, and treatment), is regulated by the Water Services Act No. 108 of 1997 (WSAt). The WSAt defines the roles and responsibilities of WSP's and WSA's. The Act requires the WSA's to submit Water Services Development plans to the DWS every five years. It should include a chapter on wastewater collection, monitoring and treatment. The Act also stipulates in Chapter 2 that the Minister may promulgate regulations that prescribe national standards relating to the acceptance of wastewater into a wastewater treatment plant and standards for tariffs with respect to the water services provided (which includes the treatment of wastewater). Regulations in this regard were published in August 2002, and took effect on 1 July 2003. In terms of these regulations, a WSA or WSP can specify the quantity and quality of wastewater (that is; municipal and/or industrial wastewater) accepted into the sewerage system to ensure that the wastewater treatment plant is capable of treating the wastewater to an appropriate level. This must be done to ensure that the treated wastewater discharge quality and quantity comply with the applicable discharge standards prescribed under the NWA.

Standards and Specifications: The Water Act of 1956 regulated the discharge of treated wastewater to ensure that the receiving water environment was protected, to safeguard public health and to enable re-use of the water by other downstream users.

The three standards that were promulgated in terms of the Act were the:

- General Standards applicable to all water resources;
- Special Standards for identified sensitive water resources;
- Special Standards for phosphate, applicable to only certain sensitive catchment areas.

The *General Standards* required the removal of carbonaceous material up to a certain specified limit and included a requirement for nitrification of ammonium to nitrate to avoid ammonium toxicity in the receiving aquatic environment. The General Standards also included limits on microbiological quality by specifying no faecal coliform in the wastewater discharge. The *Special Standards* sensitive water resources included the same range of water quality constituents and properties as the General Standards. However, it posed stricter limits due to the sensitivities of certain selected catchment areas. It also placed a limitation on the total nitrogen in the wastewater discharge. The *Special Standard for phosphate* was promulgated in response to the increased eutrophication in some water bodies in the 1960s and was a consequence of the perception that Phosphorus was the limiting nutrient for aquatic plant growth.

Treatment Process Impact: The most common wastewater disinfection treatment process is the conventional chlorination (Xu *et al*., 2011). Although this process proved quite adequate for satisfying the General Standards, it is inadequate to meet the requirements of the Special Standards with regard to chlorine residual levels in the final effluent. To satisfy both microbial and chlorine residual requirements of this standard, interest has developed in chlorination process optimisation.

The implementation of regulations in terms of the NWA still focuses on the removal of organic compounds, nitrogen, phosphate and potentially pathogenic organisms via the most appropriate combinations of treatment technologies. Due to continued deterioration of South Africa's water resources quality, changing wastewater characteristics and increased industrial waste generation, ***future discharge standards can be expected to be stricter.*** This is evident, for example, when considering the limits placed on metals in treated wastewater discharges and the inclusion of limits on organic compounds such as phenols. The DWS issues each wastewater discharge authorisation on its own merit and justifiable motivation based on economic, socio-political or technology grounds are considered, of which may allow a relaxation of the discharge standards to be authorised. In many instances, a phased approach is adopted to ensure continual environmental improvement.

2.3 OVERVIEW OF WASTE WATER TREATMENT OPERATION AND PERFORMANCE IN SOUTH AFRICA

2.3.1 Wastewater Management Overview

South Africa has built a substantial wastewater management industry that comprises approximately 970 treatment plants, extensive pipe networks and pump stations, transporting and treating an mean of 7 589 000 kilolitres of wastewater on a daily basis. The Country runs a prominent wastewater treatment business with a capital replacement value of >R 23 billion and an operational expenditure of >R 3.5 billion per annum. Limpopo municipalities own and operate 31 small, medium, large and macro-sized wastewater treatment works (WWTWs), as well as 31 plants that remain undetermined in capacity (DWA, 2009).

Recent investigations and audits reveal that the situation with regard to wastewater treatment and compliance with the respective Water Acts must be addressed as a matter of urgency. In the Minister's speech to Parliament on 11 March 2008 and her opening address at the WISA Conference in May 2008, she expressed her concern about the state of rivers and the status of wastewater treatment in the Country. She announced a number of measures underway and additional to the hands-on support already in place to municipalities. Some of these measures included (DWA, 2009):

- The initial audit was extended to all wastewater treatment plants;
- Special attention had to be given to the regulation of the sector, which includes accountability, performance monitoring and legal intervention;
- Continuous one-on-one intervention.

The function of wastewater treatment lies primarily with Water Service Authorities (WSA) and their Water Service Providers (WSP) to operate and maintain the physical infrastructure and the chemical/biological processes. As Sector Leader, the DWS has an oversight and regulatory role. The DWS is intensifying its efforts to determine and improve the status of WWTWs in South Africa. An extensive assessment and intervention plan is geared towards assisting WSA's/WSP's to improve their technical proficiency and legal compliance with effluent discharge specifications. Mobilisation of all necessary resources, funds and political commitment is required to rectify cases of non-compliance (DWA, 2009).

The need for competent Water Service Authorities (WSA) and Providers (WSP) was highlighted by the Minister of the DWS in her opening address of the National Water Summit in March 2008, themed "*Water Service Sustaining Lives and Enabling Growth*". She expressed her concern about the capacity constraints and skills gap, as well as the shortfall in funding in terms of developing new and maintaining and operating existing municipal infrastructure. She confirmed that DWS is supporting and building capacity in municipalities via various sector initiatives such as Siyenza Manje, introduction of international expertise and programmes such as Masibambane. Currently, support measures are being reformed in terms of the new Local Government Support model, which places an emphasis on "regulatory driven support" in order to ensure legislative compliance (DWA, 2009).

2.3.2 Effluent Quality Compliance

A national survey covering a selected sample of wastewater treatment plants (51) throughout South Africa to include the range of sizes of plants and different treatment technologies was conducted to obtain information on the status quo of wastewater treatment in South Africa. One of the key findings was that the most problematic unit process is ***disinfection***. More than two thirds of the plants equipped with disinfection or attempting to disinfect the treated wastewater were experiencing problems (Golder Associates Africa and Zitholele Consulting, 2006b). Highlights of this study include:

- Most of the plants do not regularly measure the effectiveness of the chlorination, which relates to the lack of information resources available to plant operational staff.

- Inadequate disinfection or failure to disinfect treated effluent discharged into a public stream can have a severe impact on downstream water users, especially if the maturation ponds are bypassed.

The graph below provides an indication of compliance trends for the various provinces based on the percentage of WWTWs that are non-compliant for the "bacteriological quality" (health related) parameter. This is based on the final effluent monitoring data received for the period 2008 to 2009. E. coli was found to be a highest non-complying parameter amongst other non-complying parameters (Manus & Van der Merwe-Botha, 2010).

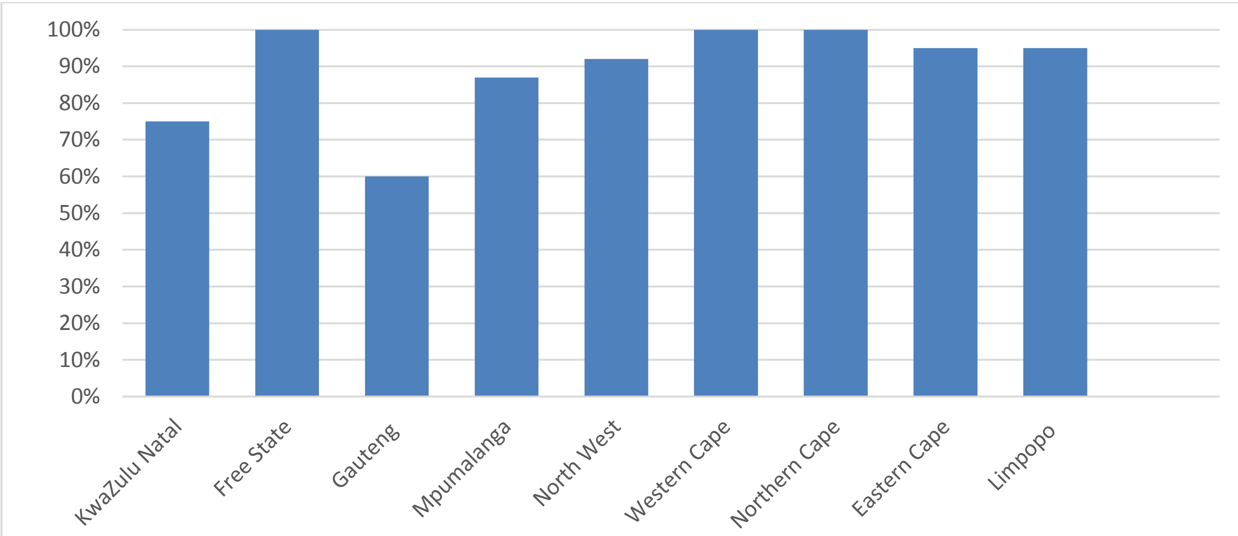

Figure 2-1: Percentage of WWTWs non-compliant for "bacteriological quality" (health related) (Manus & Van der Merwe-Botha, 2010)

The introduction of the Blue and Green Drop (incentive-driven) initiative contributed significantly and positively to municipal awareness creation, information collation and as a catalyst to facilitate the appropriate steps by the municipalities to increase wastewater performance and/or to rectify situations of non-compliance. Chasing a "green drop" or staying clear of a "purple drop" has become a target for most municipalities and the process is gaining momentum as the DWS's approach of regulatory driven support is intensifying (DWA, 2009).

The Green Drop Certification Process initiative is aimed at solving the problems of non-compliance of municipal wastewater treatment service providers by means of the South African Water Acts. The aim is to treat wastewater to a disposable quality that will minimize risks to receiving water bodies and human health. This process is driven by strengthening the regulatory approach, while at the same time refocusing the Local Government in a manner that is more responsive to regulatory imperatives (Adewumi, Ilemobade & Van Zyl, 2010).

2.4 CHLORINE DISINFECTION

At a water treatment works and wastewater treatment works, the disinfection is expected to satisfy the following three requirements (Marhaba, 2009):

1. Inactivation of the pathogenic and other harmful microorganisms in water. This is primary disinfection.

2. Disinfection residual maintenance in the distribution system. This is secondary disinfection applicable to drinking water supply.

3. Keeping the amount of by-products to a minimum.

Different disinfectants offer different performances towards the achievement of these three requirements. This is mainly because the characteristics of a disinfectant that makes it suitable for each of the three requirements are not the same (Marhaba, 2009). Today the following five disinfection agents are most commonly used for drinking water treatment:

1. *Free chlorine* is a strong oxidant that rapidly kills most of the microorganisms. It is also by far the most commonly used disinfection agent (Li *et al*., 2013). To lower the cost and, more importantly, to avoid the danger of the release of toxic chlorine gas, a relatively inexpensive sodium hypochlorite solution, which releases free chlorine upon dissolution in water, is used (Marhaba, 2009).

2. *Combined chlorine* (*chloramines*) is not a very strong oxidant, but it is used for its ability to provide longer-lasting free chlorine residual after disinfection.

3. *Ozone* is the strongest oxidant in the list and it also provides control over taste- and odour-producing compounds such as methyl isoborneol and geos-min. Use of ozone as a disinfection agent is becoming increasingly common (Marhaba, 2009).

4. *Chlorine dioxide* is also a fast-acting disinfection agent (Hornstra, Smeets & Medema, 2011), but it is not often used because of the possibility of the production of excessive amounts of chlorite, which is regulated by USEPA under the stage-2 disinfectant/disinfection by-products (D/DBP) rule.

5. *UV light* disinfection uses electromagnetic radiation. This method has two disadvantages: water must have a low level of colour for it to work efficiently and it does not leave any residual disinfectant (Marhaba, 2009).

2.4.1 Disinfection Methods (EPA Victoria, 2009)

The EPA Victoria guideline for environmental management outlines the following method for disinfection of treated wastewater:

- chemical (for example, chlorination, ozonation);
- physical (for example, ultraviolet radiation, microfiltration); and
- biological (for example, detention lagoons).

2.4.1.1 Chemical

Chlorination

Chlorine is used to disinfect wastewater in either gaseous form (Cl_2), or as hypochlorite salts. All forms of chlorine react with water to produce hypochlorous acid (HOCl), which rapidly dissociates to form the hypochlorite ion according to the following reaction:

$$\mathbf{HOCl \leftrightarrow OCl^- + H^+} \qquad \mathbf{2\text{-}1}$$

In addition to HOCl and the hypochlorite ion (OCl^-), chlorine may also be found in the form monochloramine (NH_2Cl) and dichloramine ($NHCl_2$). The dominant form of chlorine depends on the combination of parameters such as temperature, pH and ammonia concentrations. As pH increases, so too does the proportion of hypochlorite ion relative to hypochlorous acid, while higher ammonia concentrations tend to increase monochloramine.

Knowledge of the dominant form of chlorine in a particular disinfection process is important. With the differing forms come varying oxidising strengths and thus biocidal efficiencies. The chlorine disinfection process occurs primarily through oxidation of cell walls, leading to cell lysis (bacterial) or inactivation of functional sites on the cell surface. Hypochlorous acid (HOCl) is the most potent of the four main oxidising forms (Lim *et al.*, 2010).

In addition to differences in oxidising strengths between forms of chlorine, the disinfection effectiveness varies across the range of microorganisms. Protozoans, helminths and viruses are the most resistant, followed by bacterial pathogens, with each species varying in resistance.

Chlorine is very effective against enteric bacteria, such as E. coli, but less effective against other bacterial species (Queensland Department of Environment and Heritage, 1993). Therefore, with the use of E. coli to estimate disinfection efficiency one also needs to consider the relative sensitivities of the different pathogen groups. Effective chlorine disinfection depends on the correct combination of pH, chlorine concentration and contact time, as well as the levels of ammonia and suspended solids. The presence of reducing agents will act to decrease chlorination efficiency.

One disadvantage with chlorine disinfection is that free and combined chlorine residues are toxic to aquatic organisms. There is also potential for the formation of organo-chlorinated derivatives. These derivates are of particular concern, as they tend to be relatively toxic, persistent and bioaccumulative.

However, in spite of the apparent ability to form such compounds, the operational results from major sewage treatment plants show that the actual levels of these compounds in the treated wastewater are very low.

Dechlorination techniques will remove all or part of the total combined chlorine residual left from chlorination. This is achieved by using either chemical or natural processes (such as detention lagoons). However, dechlorination has no effect on the quantities of toxic chlorinated organic compounds present in the final discharge.

Ozonation

Disinfection by ozonation is achieved by using the formation of free radicals as oxidising agents. Ozonation is more effective against viruses and bacteria than chlorination, yet problems occur with effective bactericidal action when conditions are not ideal.

The low solubility of ozone in water is the main factor that greatly reduces its disinfection capacity and any ozone residual produced rapidly dissipates as a consequence of its reactive nature. The absence of a lasting residual may also be seen as a disadvantage as this may allow possible microbial re-growth and make it difficult to measure the efficiency of the disinfection process.

2.4.1.2 Physical

Ultraviolet radiation

The disinfection of treated wastewater via ultraviolet (UV) radiation is a physical process that principally involves passing a film of wastewater within close proximity of a UV source (lamp). The efficiency of UV disinfection depends on the physical and chemical water quality characteristics of the wastewater prior to disinfection. With a better quality of wastewater comes a more efficient UV disinfection process.

The advantage of the UV disinfection process is that it is rapid and does not add to the toxicity of the wastewater. There have been no reports of by-products produced by UV disinfection that adversely impact on the receiving environment.

UV disinfection does not result in a lasting residual in the wastewater. This is a disadvantage when wastewater must be piped or stored over significant distances and time (particularly relevant to re-use schemes) as re-growth of the microbial population is considered a risk.

Membrane filtration

Membrane technologies disinfect treated wastewater by physically filtering out microorganisms. This disinfection process does not require the addition of reactive chemicals and as such, no toxic disinfection by-products are produced.

Key membrane technologies include:

- reverse osmosis;
- ultrafiltration;
- nanofiltration; and
- microfiltration.

Microfiltration is the most commercially viable technology for the disinfection of treated wastewater. The wastewater passes through membrane fibres, hollow cylinders permeated with millions of microscopic pores. These pores allow wastewater to flow through the same fibres that act as a physical barrier to particles and microorganisms.

Microfiltration efficiently reduces particulates, bacteria and a range of viruses, algae and protozoans. Protozoa are generally larger than 0.2 micron and are removed effectively by microfiltration, giving this method an advantage over other technologies. Viruses larger than 0.2 micron (which includes most enteric viruses) are also reduced effectively.

The main disadvantages associated with microfiltration include the potentially high capital costs, the resultant concentrated backwash with significant microbial contamination, and the handling and management of the contaminated chemicals produced by the periodic cleaning of the membranes.

2.4.1.3 Biological

Lagoons

The storage of secondary treated wastewater in pondage systems (nominally 30 days) allows natural disinfection to take place before discharging or re-using the treated wastewater. Natural disinfection can occur via sunlight and/or natural microbial die-off. Natural disinfection processes can be affected by a number of factors such as the:

- turbidity of the wastewater, as it affects sunlight penetration;

- amount of suspended matter in the water, as viruses and bacteria may be shielded from the rays of the sun by being absorbed into surface pores; and

Temperature, pH, adsorption and sedimentation further influence the natural disinfection and inactivation processes occurring in wastewater stored in lagoons. The ability of ponds to remove or reduce the number of pathogens depends on such factors as the load of incoming solids and microorganisms, temperature, sunlight and pond design related to detention time.

Re-infection of ponds by bird populations can also pose a problem for operators. Algal blooms in the ponds over summer will also reduce the efficiency of the natural disinfection process. Systems using only detention do not typically result in a Class A effluent and are unsuitable as the sole means of pathogen reduction for high contact uses.

2.4.2 Disinfection methods comparison

The following Table 2-1 highlights the comparison of disinfection methods on effectiveness, practicality, reliability and their adverse effects.

Table 2-1: Comparison of disinfection methods (Source: modified from EPA Victoria, 2009)

Consideration	Chlorine	Ozone	UV	Micro-filtration	Detention Lagoons
Effectiveness against					
Bacteria	high	high	high	high	medium-high
Viruses	low to medium	high	high	medium to high[1]	high if detention>14 days
Parasites	low	high	not fully assessed	high	high if detention >30 days
Practicality					
Process control	well developed	developin g	developin g	developing	well developed
Complexity	simple to moderate	complex	simple to moderate	simple to moderate	simple
Maintenance and cleaning	low to moderate	moderate to intensive	intensive	intensive	low to moderate
Reliability					
	high	high	medium	medium	medium to high
Costs (dependent on size of the plant)					
Operation	medium[2]	medium[2]	medium[2]	high	low
Capital, (small to medium plant)	medium	high	low to medium	high	low to medium (reflects land value)
Capital, (medium to large plant)	low to medium	high	medium to high	high	medium to high (reflects land value)
Adverse Effects					
Safety risks: transportation	yes	no	no	no	no
Safety risks: on-site	substantia l	moderate	minimal	minimal (high noise)	minimal
Fish and macro-invertebrate toxicity	toxic [3]	unlikely	no	no	potential toxicity from algae
Formation of toxic by-products	potential	unknown	unknown	none	potential toxic algal by-products
Disposal of cleaning products	no	no	yes	yes	no
High energy consumption	no	yes	yes	yes	no

2.5 FACTORS THAT INFLUENCE THE ACTION OF DISINFECTANTS

As discussed above, different disinfectants have different characteristics that give them certain advantages or disadvantages over one another. However, there are many other influencing factors that govern the choice of the right disinfectant. The following are some of the important factors that must be considered:

1. ***Contact time*** is perhaps the most important of all the factors that influence the disinfection process. In any given concentration of disinfectant, the degree of disinfection achieved is directly proportional to the contact time (Marhaba, 2009, Lenntech, 2012). That is, the extent of inactivation is greatly affected by the duration of exposure of microorganisms to disinfectants (Kim *et al*., 2013). The formula below represent the rate of change in organism concentration with time *dNt/dt*:

$$\frac{dN_T}{dt} = -kN_t \;\; or \;\; In\frac{N_t}{N_0} = -kt \qquad 2\text{-}2$$

Where:

t = time

k = inactivation rate constant (1/time units), which can be obtained by plotting –ln($Nt/N0$) against the contact time t

Nt = number of microorganisms at time t

$N0$ = number of microorganisms at time t = 0

2. ***Concentration of disinfectant*** governs the inactivation rate constant *k*. This relationship is explained by the Watson equation (Marhaba, 2009; Rauen *et al*., 2012).

$$k = k'C^n \qquad 2\text{-}3$$

Where:

k' = die-off constant

C = disinfectant concentration

n = dilution coefficient

In addition, the magnitude of the residual concentration of viable total coliform bacteria is dependent on the initial concentration of chlorine, suggesting that complete inactivation of particle-associated organisms is possible by establishing an appropriate aqueous concentration and contact time in a disinfection system (Dietrich *et al.,* 2007).

3. ***Temperature*** is another important factor that influences the degree of disinfection achieved. Chlorine disinfection efficacy decreases with decreasing temperature (Page *et al.*, 2009). A form of the Van't Hoff–Arrhenius equation can explain the effect of temperature (Marhaba, 2009).

$$In\frac{t_1}{t_2} = \frac{E(T_2 - T_1)}{RT_1T_2} \qquad \text{2-4}$$

Where:

$T1$, $T2$ = temperatures (unit, K)
$t1$, $t2$ = time to achieve given percentage kill at $T1$ and $T2$, respectively
E = energy of activation (J/mole or cal/mole)
R = universal gas constant (8.3114 J/mole K or 1.99 cal/mole K)

Today, the influence of temperature on the rates of chemical reactions is usually interpreted in terms of what is known as the *Arrhenius equation*. According to this equation, a rate constant *k* is the product of *pre-exponential factor A* and an exponential factor:

$$k = Ae^{-E_a/RT} \qquad \text{2-5}$$

The exponential factor involves the temperature *T*, the gas constant *R* and energy E_a, which is known as the *activation energy*. The pre-exponential factor A is known formerly as the "frequency factor," but since its dimensions are the same as those of the rate constant, it is a frequency only in the case of a first-order reaction (Laidler, 1987).
Although the Arrhenius equation is usually used to interpret kinetic data, the problem of temperature dependence was one of much uncertainty and controversy in the past. However, Arrhenius removed this uncertainty when he pointed out that the magnitudes of

the temperature effects on rates are usually much too large to be explicable on the basis of how temperature affects the molecular translational energies or, in the case of a reaction in solution, how the temperature affects the viscosity of the solvent. Equilibrium is established between normal and active reactant molecules, and the Arrhenius equation was accepted because it provides an insight into how reactions proceed (Laidler, 1987).

4. ***The Types of organisms*** present in water influences the action of disinfectant and also the choice of the best disinfectant. The nature and condition of microorganisms also affect how effectively the disinfectant will work (Li & Zhang, 2013; Li *et al*., 2011). For example, older bacterial cells that have developed a slime coating are killed at a much slower rate compared to the rate of killing growing, viable cells. Viruses and protozoa may have considerably different killing rates with each disinfectant. Therefore, sometimes a combination of chemical disinfectant and heat or UV radiation is used for better efficiency.

5. ***Constituents in the effluent*** will impact disinfection. For example, turbidity will reduce the effectiveness of disinfectants by protecting entrapped bacteria. Chemical substances in the water, e.g. iron, manganese, hydrogen sulphide and nitrates, often react with disinfectants, thereby limiting disinfection potency. Existing knowledge regarding the application of chlorine in associated fields has shown that suspended solids or particles and organics in wastewater are able to provide protection to microorganisms (Winward *et al.*, 2008). Several reports have described problems in water and wastewater chlorination; for example, when poor disinfection was observed while sufficient disinfectant was present (Amiri *et al.*, 2010). Dietrich *et al.* (2003) report, however, that chlorine is capable of penetrating particles in wastewater by radial diffusion. They demonstrated that the degree to which chlorine penetrates particles in wastewater is influenced by a variable initial chlorine concentration (mg L^{-1}) at a fixed dose (mgmin L^{-1}). Chlorine penetration of particles up to 145 mm is reported.

6. ***Chlorine demand***: Since chlorine is a very reactive chemical, it also reacts with other substances present in the water (Dai *et al*., 2013), such as organic and inorganic material,

which may include reduced metals, sulphides, bromine ions, organic and inorganic nitrogenous compounds (Metcalf & Eddy, 1991). These compounds create a chlorine demand and free chlorine will only be available once the demand by these compounds has been satisfied. Satisfying the chlorine demand by other substances apart from disinfecting microorganisms is called breakpoint chlorination and is wasteful because more chlorine is consumed than is required for disinfection alone (Pretorius, 1999; Winward *et al.*, 2008). A consequence of this is that the wastewater treatment process increases the cost of chlorine required for disinfection. Unfortunately, total chlorine demand currently determines chlorine dosage in most water treatment processes and hence, to adequately disinfect wastewater, higher disinfectant concentrations are employed to kill pathogenic microorganisms.

Chlorine demand is defined as the difference between the initial chlorine concentration and the chlorine residual after a specified contact time, t (or as C_0–C_t, where C_0 is the initial free chlorine concentration and Ct is the free chlorine concentration at contact time (t) (Helbling & Van Briesen, 2007; Winward *et al.*, 2008).

7. ***Mixing***: Longly (1978) evaluated turbulence factors in chlorine disinfection of wastewater in addition to the above-mentioned factors. Longly (1978) found that the inactivation of microorganisms achieved during disinfection may not always be adequately predicted by the above-mentioned factors (especially chlorine residual and contact time), but can be predicted by the mixing of chlorine with the incoming wastewater. To date, the impact of mixing on chlorine disinfection has not been directly researched and/or applied. Longly (1978) indicates that before the chlorine is mixed throughout the mass of incoming wastewater, reactions competing with the disinfection process result in the formation of chloramines, other by-products and rapid depletion of free chlorine.

The inactivation of microorganisms in water by disinfection processes is clearly influenced by a variety of factors, including type and physiological condition of microorganisms, type of disinfectants, physical and chemical water quality parameters, such as pH, temperature, inorganic and organic constituents, particulates, and hydraulic conditions such as reactor design and mixing conditions (Shin & Sobsey, 2008).

2.6 THEORY OF DISINFECTION

A chlorine compound is used for disinfection processes because it is strong oxidizing agent (Li *et al.*, 2013; Lim *et al.*, 2010). However, oxidation is not the only process that governs disinfection, more interactions occur simultaneously and contribute and/or influence the inactivation of microorganisms in water.

2.6.1 Disinfection with Chlorine (Free and Combined)

Sodium hypochlorite and solid calcium hypochlorite solutions are widely used to avoid the risk or release of toxic chlorine gas. The concentration of hypochlorite or any other oxidizing disinfectant is often expressed as *available chlorine*, which refers to the relative amount of chlorine present in chlorine (under pressure liquid form) or hypochlorite. Upon application, chlorine gas quickly hydrolyses to form hypochlorous acid (HOCl) and hydrochloric acid (HCl) (Metcalf & Eddy, 1991; Debordea & Guntena, 2008; Nanayakkara *et al.*, 2012; Rauen *et al.*, 2012).

$$\boldsymbol{Cl_2 + H_2O \leftrightarrow H^+ + Cl^- + HOCl} \qquad 2\text{-}6$$

For this reaction, the equilibrium constant is as follows:

$$\boldsymbol{K_H = \frac{[H^+][Cl^-][HOCl]}{Cl_{2(aq)}}} \qquad 2\text{-}7$$

Where:

K_H = equilibrium constant (mole/L^2): $K_H = 4.48 \times 10^4$ at 25^{O}C

Henry’s law describes the dissolution of gaseous chlorine to form dissolved molecular chlorine (Marhaba, 2009).

$$\boldsymbol{Cl_{2(g)} = \frac{Cl_{2(aq)}}{H} = \frac{[Cl_{2(aq)}]}{P_{CL2}}} \qquad 2\text{-}8$$

Where:

$8[Cl_{2(aq)}]$ = molar concentration of Cl_2

P_{Cl2} = partial pressure of chlorine in atmosphere

H = Hennry's law constant (mole/L atm)

T = temperature (K)

HOCl is a weak acid and it dissociates further to produce hypochlorite ions (OCl^-) and hydrogen ions.

$$\mathbf{HOCL \leftrightarrow OCl^- + H^+} \qquad \textbf{2-9}$$

For this reaction, the acid dissociation constant is as follows:

$$\boldsymbol{K_a = \frac{[OCl^-][H^+]}{[HOCL]}} \qquad 2\text{-}10$$

Where:

K_a = acid dissociation constant (model/L)

In the presence of certain constituents in water, chlorine can react and transform to less effective chemical forms, referred to as combined chlorine. In the presence of ammonium ions, free chlorine undergoes the following step-wise reactions to form monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3). These formations are also pH-dependent (Metcalf & Eddy, 1991; Marhaba, 2009; Dai *et al*., 2013).

$$\mathbf{NH_4^+ + HOCl \leftrightarrow NH_2Cl + H_2O + H^+} \qquad \textbf{2-11}$$

or

$$\mathbf{NH_{3(aq)} + HOCl \leftrightarrow NH_2Cl + H_2O \ \ (pH > 7)} \qquad \textbf{2-12}$$

$$\mathbf{NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O \ (not\ favoured\ at\ a\ high\ pH)} \qquad \textbf{2-13}$$

$$\mathbf{NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O} \qquad \textbf{2-14}$$

- *Free available chlorine* is the sum of [HOCl] and [OCl^-].
- *Combined chlorine* is the sum of the three chloramines formed in the reactions above.
- *Total available chlorine* is the sum of free chlorine and combined chlorine.

The dominant form of chlorine depends on the combination of parameters, such as temperature, pH and ammonia concentrations. As the pH increases, so too does the proportion of hypochlorite ion relative to hypochlorous acid, while higher ammonia concentrations tend to increase monochloramine (EPA Victoria, 2009; Amiri, 2010).

Breakpoint chlorination is a phenomenon in which all the ammonium ions disappear and the solution possesses free chlorine residue. It occurs when the molar ratio of chlorine to ammonia is greater than 1.0. Under ideal conditions, at breakpoint chlorination, the reduction of chlorine and oxidation of ammonia occurs at a 2:1 ratio. Further addition of chlorine results in more and more free available chlorine. This phenomenon is very important in calculating the chlorine dosage to maintain the chlorine residue in contact with microorganism for effective inactivation (Marhaba, 2009 & Fisher *et al*., 2011).

Figure 2 shows the curve for chlorine dosage vs. chlorine residue to explain the phenomenon of breakpoint chlorination.

- Stage 1: Chlorine is reduced to chlorides by metallic ions and compounds that are oxidized easily (Fe^{2+}, H_2S, etc.).
- Stage 1 and Stage 2: Chlorine reacts with ammonia to form chloramines, which are weak disinfectants.
- Stage 2: The nitrogen trichloride formation reaction is favoured and the chloramines are consumed in the reaction with free chlorine. In this zone, nitrogen gas is formed, which leaves the system and breakpoint chlorination is reached.
- Stage 3: Free chlorine residue is observed in water and further addition of chlorine only increases the residue concentration.

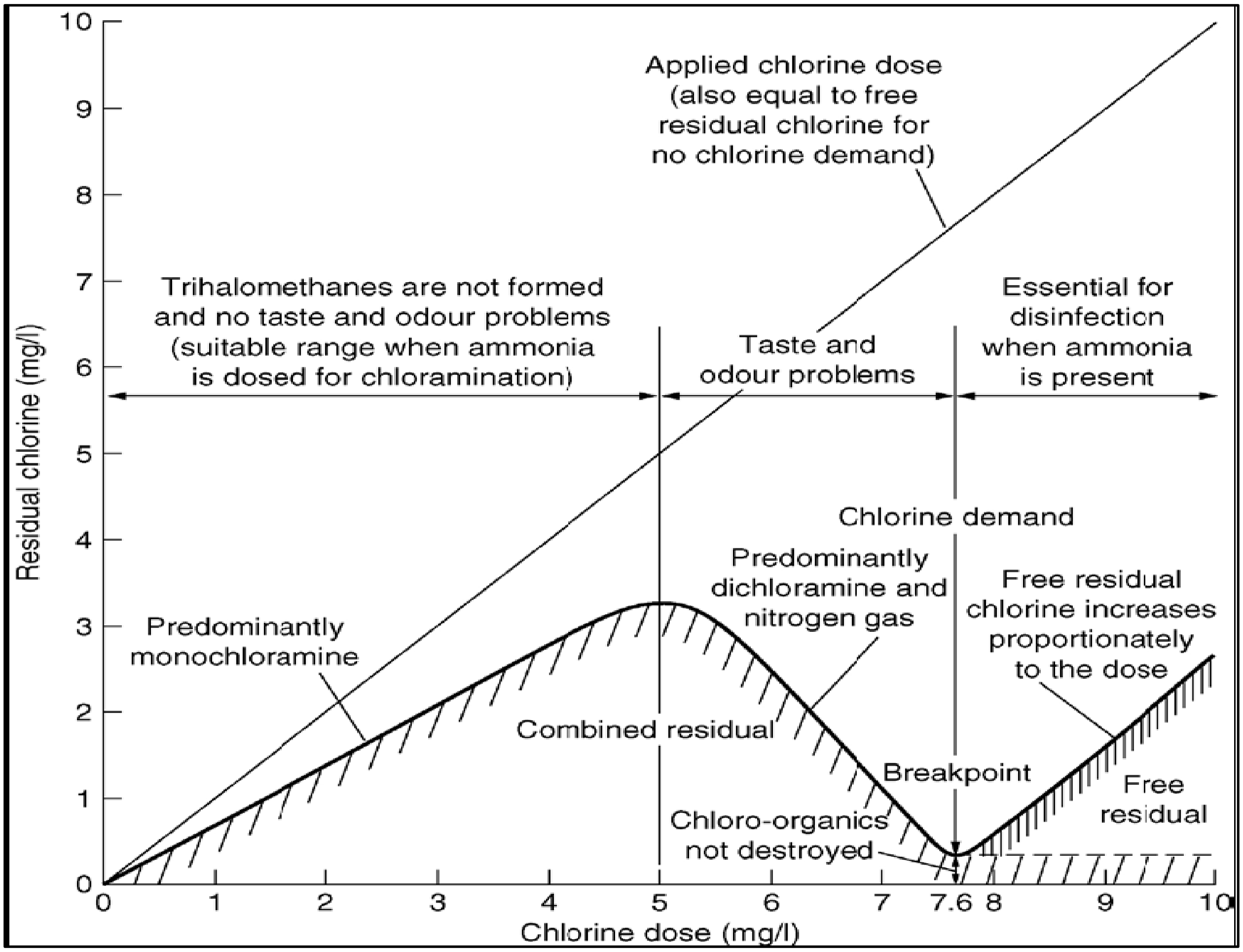

Figure 2-2: Theoretical breakpoint chlorination (Marhaba, 2009).

2.6.2 Kinetics of Chlorine reaction

Chemical reaction kinetics deals with the rates of chemical reaction and with how the rates depend on factors like concentration, contact time and temperature. Kinetics looks at the time it takes for the reactant to be consumed. A reaction in the solution can be thought of as involving three steps:

i. diffusion of the reactant;

ii. actual chemical transformation; and

iii. diffusion of the products away from each other (Laidler, 1987).

2.6.2.1 Diffusion reaction

For the process of disinfection with which this study is concerned, the diffusion of chlorine into microorganism should be much faster than the chemical transformation (Laidler, 1987).

Nanayakkara *et al*., (2012) assume that the disinfection of E. coli is primarily due to electro-chlorination. Therefore, the following reaction between chlorine and E. coli can be used:

$$\boldsymbol{nA + mB \rightarrow D} \qquad \textbf{2-15}$$

where A = E. coli; B = Chlorine; m, n = Constants; D = Products.

As such, the reaction rate based on the disinfection of E. coli can be written as:

$$\boldsymbol{r_{A= -KC_{A}\,.\,C_B^m}} \qquad \text{2-16}$$

where C_A *= Concentration of E. coli, Count/100 mL;* C_B *= Concentration of total chlorine, mg/L; k = Reaction rate constant, [(1/min)_(L/mg)m].*

The mass balance in the control volume for the E. coli can be written as follows:

Accumulation = In - Out - Loss + Production 2-17

Nanayakkara *et al*., (2012) further indicates that since no accumulation or production of E. coli is expected, the above equation can be simplified to:

In - Out = Loss 2-18

When the E. coli concentration in the influent is high, the rate of disinfection is low and the chlorine concentration has a greater effect on the disinfection efficiency (Nanayakkara *et al*., 2012). Jeong *et al*. (2006) reported a reduction in the disinfection efficiency with an increase in the initial population of E. coli in the electrochemical inactivation of E. coli in KH_2PO_4. Their study suggests that the consumption of oxidants is higher if the initial concentration of bacteria was high. They concluded that the chlorine produced is consumed by the microorganisms. Ammonia plays a critical role during chlorination because of its competition with antibiotics for free chlorine to form combined chlorine, which reacts slowly with these antibiotics (Li & Zhang, 2013).

The inactivation of E. coli in an ideal batch or plug flow reactor can be described by a first order kinetic reaction (Smeets *et al*., 2006):

$$\frac{N_t}{N_0} = e^{-R_e C t} \qquad 2\text{-}19$$

where N_0 and N_t are the number concentrations of organisms at 0 and t min respectively and R_e is the inactivation rate constant (based on natural logarithm) in l /(mgmin).

2.6.2.2 Chemical Transformation

Similar to other disinfection processes, chlorination presents certain disadvantages in spite of its broad use and its benefits for the improvement of microbial water quality (Debordea & Guntena, 2008):

i. Due to its pH-dependent aqueous chemistry, various species of chlorine (HOCl, ClO, Cl2, etc.) may be present in a solution. These forms of chlorine show significant differences in their reactivity with microorganisms and micropollutants. Therefore, variability in oxidation or disinfection efficiency can be observed depending on the pH of the water.

ii. Chlorine interacts with dissolved natural organic matter (DNOM). Numerous so-called disinfection by-products (DBPs) can result from the reaction of chlorine with DNOM. Among these DBPs, there are trihalomethanes (THMs) and haloacetic acids (HAAs), which are most common. Accordingly, chlorinated effluent from wastewater treatment is a high source of concern for DBPs (Wu *et al.,* 2010).

iii. Because organic micropollutants are typically not mineralised, numerous transformation products can be formed as a result of the oxidation of organic compounds during water chlorination processes.

For most of the chlorination reactions, the elementary reaction can be formulated as:

$$\mathbf{HOCl + B \rightarrow products,} \qquad \mathbf{2\text{-}20}$$

where B is an organic or inorganic compound.

That is,

During aqueous chlorination, hypochlorous acid reacts with NH_3 to generate NO_3^- and N_2 for $[HOCl] > [NH_3]$. This oxidation results from successive reactions, which firstly induce chloramine mono-, di- and tri-chloramines formation:

$$\mathbf{NH_3 + HOCl \rightarrow NH_2Cl + H_2O;} \qquad \mathbf{2\text{-}21}$$

$$\mathbf{NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O;} \qquad \mathbf{2\text{-}22}$$

$$\mathbf{NHCl_2 + HOCl \rightarrow NCl_3 + H_2O:} \qquad \mathbf{2\text{-}23}$$

As in the case of the inorganic compounds shown above, hypochlorous acid is also the dominant reactive species for the reaction with the majority of organic compounds. The following three kinds of reactions of hypochlorous acid with organic compounds can be described:

(i) oxidation reactions,
(ii) addition reactions to unsaturated bonds,
(iii) electrophilic substitution reactions at nucleophilic sites.

Hypochlorous acid thus presents high selectivity towards organic micro-pollutants and its reactivity is usually restricted to limited sites (reducing, nucleophilic and unsaturated sites). Hypochlorous acid generally induces small modifications in the parent compound’s structures, leading to more oxidised or chlorinated molecules (Debordea & Guntena, 2008).

2.6.3 Mechanism of Disinfection

The precise mechanism of microorganism inactivation by chlorine has not been fully elucidated in the literature. However, that the bacterial cell membrane undergoes changes in permeability in the presence of chlorine and that the membrane is an important factor in determining bacterial resistance to chlorine disinfection (Winward *et al*., 2008). The action of a disinfection agent can be explained through the following five mechanisms (Marhaba, 2009):

1. *Cell wall destruction* that results in cell lysis and death. Chlorine hydrolyses the cell, causing mechanical disruption.
2. *Cell permeability alteration* that can result in a loss of selective permeability of the cytoplasmic membrane, allowing nitrogen, phosphorous, and other vital nutrients to flow out. Chlorine alters the cell wall permeability, resulting in lethal damage to the cell.
3. *Alteration of the colloidal nature of the protoplasm* by heat, radiation and highly alkaline or acidic agents that cause coagulation or denaturing of the cell protein, which in turn produces permanent cell damage. Chlorine compounds can alter the colloidal nature of the protoplasm.
4. *Deoxyribonucleic acid* (*DNA*) *or ribonucleic acid* (*RNA*) *alteration* that results in disruption of the replication process (because DNA and RNA carry genetic information for reproduction) and inactivation of the organism.
5. *Inhibition of enzyme activity* by strong oxidizing agents, altering the enzyme's chemical properties. Chlorine is capable of causing inactivation of enzymes.

The free chlorine agents, HOCL and OCl^-, are capable of inactivating microorganisms. Due to the complexity of the disinfection process, it is difficult to pinpoint the exact mechanism. The presence of chlorine suggests that it would be the major disinfection mechanism (Nanayakkara *et al*., 2012). Free chlorine is responsible for the reaction with antibiotics during the rapid stage (first 5 Second-1 minute), whereas combined chlorine react with antibiotics in the subsequent slow stage (Le & Zhang, 2013).

Therefore, knowledge of the dominant form of chlorine in a particular disinfection process is important. With the differing forms come varying oxidising strengths and thus biocidal efficiencies. Hypochlorous acid (HOCl) is the most potent of the four main oxidising forms. It is well established that the free chlorine species can react with various amino acids in the virus capsid proteins, as well as with the nucleic acid protected by the capsid. However, the actual limiting step (that is, the molecular target and its level of damage) responsible for inactivation is not yet known (Li *et al*., 2011).

In addition to differences in oxidising strengths between forms of chlorine, the disinfection effectiveness varies across the range of microorganisms. Protozoans, helminths and viruses are the most resistant, followed by bacterial pathogens, with each species varying in resistance. Chlorine is very effective against enteric bacteria, such as E. coli, but less effective against other bacterial species (EPA Victoria, 2009). Therefore, the use of E. coli to estimate disinfection efficiency needs to consider the relative sensitivities of the different pathogen groups. Effective chlorine disinfection depends on the correct combination of pH, chlorine concentration and contact time, as well as the levels of ammonia and suspended solids.

2.7 TURBULENCE/MIXING FACTOR

The design and operation of a disinfection system have been and will continue to be an evolving process. There has been a significant amount of research on disinfection during the 20^{th} century (Ducost, Carlson & Bellany, 2001). However, very few studies have been conducted on turbulence and/or mixing factor effects on disinfection effectiveness. The engineering considerations surrounding the subject of chlorine mixing have been generally overlooked in the past (White, 1999).

Smeets *et al.,* (2006) in their study of inactivation of Escherichia coli by ozone under bench-scale plug flow and full-scale hydraulic conditions found that the expected inactivation based on the continuous stirred tank reactor (CSTR) method approached the observed inactivation at full-scale.

Therefore, the CSTR method should be preferred to calculate inactivation of ozone sensitive organisms such as E. coli, viruses, Giardia and Campylobacter by full-scale ozonation.
Ducoste, Carlson and Bellamy (2001) integrated a disinfection design framework approach with reactor hydraulics characterization. Their study results suggested that the predicted microbial inactivation level is sensitive to the hydraulic characterisation method. Results also showed that the disinfectant dose applied to the contactor could be reduced by 35% and still maintain the same credit for the Giardia inactivation specified standard.

Longly (1978) evaluated turbulence factors in chlorine disinfection of wastewater. He found that the inactivation of microorganisms achieved during disinfection may not always be adequately predicted by the usual factors affecting disinfection efficiency (especially chlorine residual and contact time), but could be predicted by the mixing of chlorine with the incoming wastewater. To date, the impact of mixing on chlorine disinfection has not been directly researched and/or applied. Longly (1978) indicated that before the chlorine is mixed throughout the mass of incoming wastewater, reactions competing with the disinfection process results in the formation of chloramines, other by-products and rapid depletion of free chlorine.

Dai *et al*., (2013) found that the monitoring results of their study showed that better instantaneous mixing at the chlorine injection point reduced the effect of chlorination/dechlorination on 5-day BOD levels.

The results of these studies show a wide range of inactivation kinetics, with the potential for the contact time (Ct) and the disinfectant dose applied to the contactor to be reduced while not compromising on disinfection efficiency. It is also shown that the physical mixing of the disinfectant (chlorine) with the water to be treated was essential in ensuring adequate disinfection.

In-line initial mixing has been proposed for the rapid and complete dispersion of a coagulant to happen within the first second, before the metal hydroxide precipitate can form (Kim & Lee, 2006). The importance of mixing factors was put in proper perspective by the pilot-plant work of White, (1999). This work revealed that the difference between a plug flow mix in a turbulent regime and that of a back-mixed system (one with short circuiting) amounted to about 2 logs in the reduction of coliform concentration.

2.8 COST ASSESSMENT OF DISINFECTION

Because of public health concerns, toxicity of chlorination and more restrictive discharge criteria, alternative disinfecting agents (such as ozone, ultraviolet light, hydrogen peroxide and chlorine dioxide) have been proposed for the final treatment of wastewater effluents (Tyrrell, 1995).

Freese, Bailey and Nozaic (2003) selected ozone, medium pressure UV irradiation, peracetic acid and bromine as potential candidates instead of chlorine for the disinfection of wastewater treatment and the cost assessment resulted as follows:

Table 2-2: Cost assessment of alternative disinfection dosage required to meet both the relaxed (<500 Count/100 ml) and general (0 Count/100 ml) DWS effluent discharge standards (Freese, Bailey & Nozaic, 2003).

.	**Relaxed Standard**		**General Standard**	
Disinfection	**Dose for<500 E. coli**	**c/kL Cost for <500 E. coli**	**Dose for <10 E. coli**	**c/kL Cost for <10 E. coli**
Ozone	2 mg/l	3.45	8 mg/l	9.5
UV	40 mW.s/cm^2	3.72	150 mW.s/cm^2	11.2
Peracetic acid	5 mg/l	40.0	9.5 mg/l	76.0
Bromine	6 mg/l	50.0	9.5 mg/l	79.2
Chlorine	6 mg/l	3.00	9.5 mg/l	4.75

The higher costs of Ozone as compared to the cost of chlorine for disinfection are due to the fact that the capital costs of Ozone are expensive. However, the high cost of Ozone is offset to some degree by relatively low running costs. Nonetheless, Ozone requires skilled personnel to run and maintain the Ozone generation.

Although it is clear that UV could be applied to the disinfection of wastewater, there are various factors that have to be considered when choosing this as the disinfection process. Rudd and Hopkinson (1989) indicate that although UV has been found to be an effective disinfectant, an effluent of a reasonably good quality in terms of UV absorbance or transmissivity is required in order for this method of disinfection to be feasible, both economically and technically. Furthermore, despite the fact that there is no technical limitation to the size of a UV plant, the costs of UV units tend to become prohibitive at larger facilities because of the high capital cost even though running and maintenance costs are relatively low and in fact, compare very favourably with chlorine costs in achieving the effluent discharge standard (Freese, Bailey & Nozaic, 2003). Another advantage of using UV is that it is simple to maintain and operate.

The peracetic acid method of disinfection ends up not being viable due to its high price that results in exorbitant running costs. Freese, Bailey and Nozaic (2003) in their study found that peracetic acid could achieve 100% compliance with the effluent discharge standard when used at concentrations of 5 mg/l or more. However, in meeting the Special Standard (discharge limits and conditions set out in the National Water Act, Government Gazette No. 20526) of 0 Count/100ml of faecal coliforms, it was necessary to almost double the dose of 5 mg/l.

Freese, Bailey and Nozaic (2003) found peracetic acid to be similar to chlorine for the disinfection of wastewater. However, the cost relative to chlorine is very high. Major disadvantages associated with peracetic acid disinfection is the increase of organic content in the effluent due to acetic acid (AA) and thus in the potential microbial regrowth (Kitis, 2004).

Over and above the comparative low cost of the chlorine disinfection method, the disadvantage of chlorine is that chlorine is highly toxic and thus requires more precaution during storage, handling, and shipping. Since chlorine residual that is discharged without dechlorination can be toxic to aquatic life and the discharge standard for special limits for effluent discharge into water course is 0 mg/l free chlorine, it is important to dechlorinate the final effluent that results from the current application of chlorination. This method substantially increases operating costs. Moreover, the dechlorination process involves the addition of other chemicals, such as bismuth sulphate to the effluent, thus magnifying the existing problem of polluting estuaries with foreign chemicals (Tyrrell, 1995).

Dechlorination techniques will remove all or part of the total combined chlorine residual left from chlorination. This is achieved using either chemical or natural processes (such as detention lagoons). However, dechlorination has no effect on the quantities of toxic chlorinated organic compounds present in the final discharge (EPA Victoria, 2009).

Presently, the extensive use of chlorine-based disinfection has a range of advantages, including ease of handling, measurement and control, low cost of installation and, most importantly, the controlled concentration of chlorine residual after treatment (Rauen *et al*., 2012). Due to chlorine's efficiency and relatively low capital demand, many wastewater treatment plants have applied chlorination for disinfection of treated wastewater before discharging it. However, determination of optimal doses of chlorine for chlorination and sulphite for dechlorination, which removes residual chlorine, should guarantee complete destruction of microorganisms in treated wastewater and should protect aquatic life in a receiving stream from toxic effects of active residual chlorine (Kim *et al*, 2006; MacCrehan, *et al.*, 2005).

CHAPTER 3

3 MATERIAL AND METHODOLOGY

3.1 INTRODUCTION

This chapter provides an explanation of the research design, details regarding the samples collected, instrumentation employed, means of data collection and data analysis. The research objectives are:

1. To empirically evaluate the impact of chlorine and wastewater contact time (Ct) and chlorine residual concentration on microorganism inactivation, while reducing chlorine dose and aiming not to meet chlorine demand.

2. To empirically evaluate the impact of mixing on effective disinfection at the point of chlorination.

3.2 RESEARCH DESIGN

Laboratory and field experiments were employed to explore the effect of mixing on the effectiveness of chlorine disinfection of wastewater effluent to inactivate indicator bacteria without first meeting the chlorine demand. The premise of this study is that the application of mixing at the point of chlorine dosing has a positive effect on enhancing the inactivation of microorganism (E. coli and/or Faecal Coliforms bacteria). Mixing can increase the exposure of microorganisms to disinfectant, resulting in an optimal disinfection process at a much lower chlorine level before or while chlorine is reacting with impurities that demand chlorine in wastewater effluent. Smeets *et al*. (2006) indicate that when comparing the observed inactivation kinetics in full-scale systems with inactivation kinetics determined under laboratory conditions, chlorination in the full-scale system appears to be less effective than is experienced in the laboratory. This is attributed to the suboptimal hydraulics of full-scale systems which is known to reduce the efficacy of inactivation. In this study therefore, both laboratory and full-scale experiments will be conducted.

Laboratory experiments were conducted using effluent from Burgersfort and Pampirstat Wastewater Treatment Works. Both treatment works operate secondary treatment systems that consist of screening, grit removal, primary settling, biological treatment, secondary settling and chlorination. Activated sludge serves as the biological treatment at both treatment works. The full-scale experiment was carried out at the Burgersfort wastewater treatment works which is also a secondary treatment system comprising screening, grit removal, primary settling, biological treatment, secondary settling and gas chlorination.

The methodology applied in both experiments are described below:

3.3 FULL SCALE INVESTIGATIONS

The Burgersfort wastewater treatment works in Burgersfort town, Limpopo ($S^0$24 39 52 $E^0$29 20 11.9) was monitored during the study period. Chlorine demand results, as determined by the laboratory test, were compared with the dosing concentrations applied by process controllers on site and the bacteriological quality of the wastewater discharged.

3.3.1 Description of the sample

A sample is a part or piece taken from a larger entity and is presented as representative of the whole. The objective of sampling is to collect a portion of the effluent of a sufficient volume to be conveniently handled in the laboratory and that can still be representative of the quality of the effluent being examined. Samples can either be grab or composite type, depending on the method of sampling.

The effluent sample of the secondary sedimentation tank was collected during this study. The plant which is conventional sewage treatment works treats on average 3 mega litter (Ml) of wastewater per day. It is a conventional sewage treatment works. The quality results of wastewater samples collected on monthly basis between June 2011 and October 2012 from the raw water, effluent from secondary sedimentation tanks or humus tanks and final effluent discharged into the water course were consulted during the experiment period. Samples for bacteriological analyses of the final effluent from the treatment plant were collected in sterile bottles containing 4.2ml 1% sterile sodium-thiosulphate ($Na_2S_2O_3$) to quench any remaining chlorine immediately after sampling.

New and thoroughly rinsed non-sterile 2 litre plastic bottles were used to collect samples for chemical analyses. The samples were placed in coolers containing ice packs and transported to the Lepelle Northern Water laboratory at Ebenezer Water Treatment Plant for analyses within six hours after samples were collected. Water quality analyses were conducted monthly for treatment works compliance monitoring. In other words, operational monitoring is also done for plant process control. The water quality results of these monthly compliance samples were interpreted to obtain baseline information on treatment plant performance.
Samples for bench scale investigations were collected in thoroughly cleaned non-sterile 20L polyethylene containers containing 0.2% $Na_2S_2O_3$.

All effluents samples collected were stored at room temperature in the original sample container for up to 12 hours during the course of each test. Tests were generally conducted within 6 hours of sample collection. Compliance monitoring samples collected were analysed for ammonium, nitrate and nitrite, COD, pH, turbidity, E. coli (indicator organisms) and chlorine residual.

3.3.1.1 Microbiological Analyses

Enumeration of Coliform (E. coli) was analysed by the IDEXX quanti-tray standard method, according to the South African National Accreditation Services (SANAS) accredited method equivalent to SABS method 221.

3.3.1.2 Chemical Analyses

i. pH and Turbidity

Measurements for pH and turbidity were done according to the procedures described in the Standard Methods for the examination of water and wastewater (1998), using a Metrohm 827 pH Lab, and a HACH 2100P Turbidity-meter respectively.

ii. Ammonia

Ammonium was analysed using a DR/2500 spectrophotometer

iii. Chemical Oxygen Demand

COD was determined using the colorimetric determination method 8000

iv. Chlorine Residual

Chlorine residual was analysed using a HACH pocket colorimeter. The chlorine concentration was determined by the DPD free and total chlorine methods.

v. Nitrate and Nitrite

Nitrate levels were determined by a colorimetric cadmium reduction method using a HACH Nitrate Test Kit.

All physical and chemical parameters were determined within 12 hours of effluent collection.

3.3.1.3 Full-scale experimental setup

The full-scale installation (Fig. 3.1) had chlorine dosing contact chamber/sump with a total volume of 505 litres. The average hydraulic residence time at a flow range of 62.5 m^3/h - 125m^3/h was 0.48min – 0.24min. Chlorine gas was dosed and distributed in water with diffuser plates. Sample points were placed just after the dosing chamber and at the effluent discharge point into the river. Continuous stirring was provided in the dosing chamber/sump by installed variable speed mechanical mixer/stirrer.

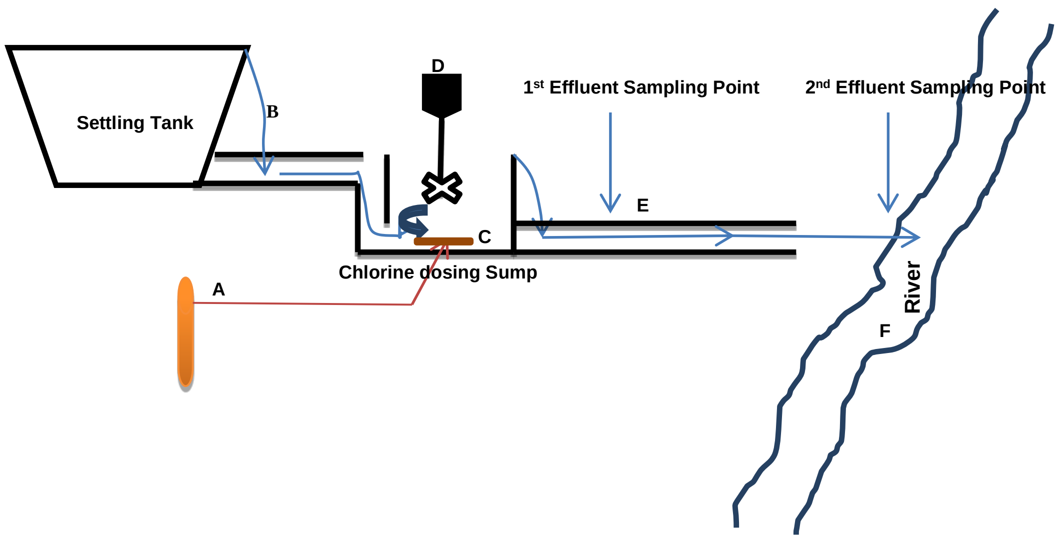

Figure 3-1: Layout of full-scale experimental setup = (continuous stirred tank reactor (CSTR)). A = Chlorine gas cylinder, B = Settles effluent overflow, C = Chlorine dosing chamber, D = Stirrer (mixer), E = Effluent open channel, F = Watercourse.

3.4 BENCH SCALE INVESTIGATIONS

3.4.1 Description of the sample

The description is the same as in section 3.31 above.

3.4.2 Chlorine solution preparation.

The chlorine solution used in the experiments were made from HTH and chlorine gas diluted with chlorine demand-free water (distilled water) to obtain a stock solution of about 600-800 mg/l free chlorine concentration measured by HACH pocket colorimeter.

3.4.3 Chlorine Demand Tests

- Two starch solution were prepared: (i) 0.025N sodium thiosulphate solution according to the standard method for the examination of water and wastewater (1998) (section 2350B (g)) and calcium hypochlorite (HTH = 65% m/v available chlorine) solutions.
- The HTH solution was standardised according to the method in the Standard Methods for the Examination of Water and Wastewater (1998) (section 2350B (g)) using 0.025N sodium thiosulphate.
- Volumetric flasks were filled with 100ml of primary effluent collected after settling tank process unit (that is; unchlorinated sewage water).
- Each flask was added with the determined volume of standardised HTH solution to give chlorine dose concentration of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 mg/l and the intervals between additions was noted to be within 1 minute.
- Immediately after adding the HTH solutions to each flask, the cap was screwed on and the flask shaken. Thereafter, the flask was kept in a dark place for 30 minutes.
- After 30 minutes, each flask was shaken again and a 10 ml sample was withdrawn and free chlorine concentration measured using a HACH pocket colorimeter.
- The chlorine demand was determined by plotting the chlorine residual (total chlorine concentration) against the chlorine added and finding the point at which either the total chlorine concentration approached zero, or the total chlorine residual started increasing *pro rata* with the chlorine addition, indicating the breakpoint chlorination and chlorine demand value.
- These chlorine demand test was done each time before starting with each batch experiment.

3.4.4 Batch Chlorination Experiments

The experiment was conducted using primary effluent poured into 5 litre dark non-transparent glass bottles and chlorinated by the addition of liquid chlorine depending on chlorine demand tests done as indicated above in 3.4.3. These samples were then used to determine the effect of the following on chlorine demand and E. coli disinfection efficiency:

- Substances present in the water i.e. Chemical Oxygen Demand (COD) and ammonium;
- Chlorine dosage concentration;
- Suspended solids (turbidity); and
- Contact time.

E. coli was used as an indicator organism because it is more faecal specific and can be analysed quickly, efficiently and cost-effectively. Furthermore, E. coli is more resilient to chlorination than other pathogens excreted in human faeces and is found more abundantly (Helbling & Van Briesen, 2007, Headley *et al.*, 2013)

The effect of substances present in the water: the primary effluent from settling tank was spiked with raw sewage to increase the concentration of the COD, Ammonia, Turbidity, Nitrate and Nitrite in the effluent.

The effect of mixing: the same chlorine concentrations were dosed into three 5 litre dark glass bottles filled up to 50% mark (that is; the bottle was half full). The mixing was provided by hands shaken vessel/bottle to simulate turbulent flow as follows:

- The first bottle was not mixed
- The second bottle was mixed in a low intensive mix by gently shaking/swivelling it upside down five times within 5 seconds.

- The third bottle was mixed in a high intensive mix by vigorously shaking/swivelling it upside down five times within 2.5 seconds.

All experiments were conducted in at least triplicate and the mean values are reported.

The above mixing methods are limited in simulating turbulent flow and do not involve the carrying out of measurements to determine variation of the flow dynamics in a shaken geometry for different operating conditions such as height, orbital shaking diameter, reactor inner diameter and fluid viscosity.

The effect of increased substance concentration on E. coli inactivation.

Suspended solids (SS) influence the effectiveness of chlorination on the targeted bacteria.

Effluent samples from a secondary settling tank were spiked with sewage raw mixed liquor to obtain a final SS concentration of 90 mg/l, which was the upper limit of the general discharge effluent quality standard (Metcal & Eddy, 1991; 2004). The follow spike ratios were 1:3 and 1:7 of influent (raw) to secondary settling (humus) tank effluent. Blank sample investigations without raw sewage spike were conducted as a background investigation.

Contact times established for the test of the effect of increased substance concentration on E. coli inactivation was a minimum of 15 min. and maximum of 60 min. These contact times were established for two reasons. First, 15 min. is the minimum contact time required by the U.S. Environmental Protection Agency (EPA) for the chlorination process (Tyrrell, 1995). Secondly, contact time of 60 min was chosen because the median contact time for chlorine disinfection in most water treatment plants is 60 min (Li *et al*., 2011).

The effect of increased contact time and increased dosing concentration on E. coli inactivation.

The study investigated three representative initial chlorine dosages of 2, 4 and 6 mg/l, which satisfy the microbial disinfection requirements as per prior chlorine demand test performed. For each dosage concentration, investigations for 20 and 40 minutes contact times were analysed under identical experimental conditions.

The effect of mixing on E. coli inactivation.

The effect of the mixing experiment was undertaken with a chlorine dosage range of 0 to 5 mg/l and a sample was taken after 1, 2 and 3 minutes of contact time. The set of three experiments under identical experimental conditions was conducted under the following mixing conditions:

- No mixing
- Mixing by gently shaking/swivelling it upside down twice within 5-7 seconds.
- Mixing by vigorously shaking/swivelling it upside down five times within 2.5 seconds.

3.5 DATA ANALYSIS

All experiments were conducted in at least triplicate. Descriptive statistical analysis was performed. Mean, range, mode and median values are reported.

Correlation for Burgersfort WWTW effluent quality with factors that affect disinfection as independent variable and Chlorine demand as dependent variable was determined.

CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 INTRODUCTION

This section contains the results of this study involving laboratory batch and full-scale experiments. The results were used to validate the study hypothesis.

4.2 FULL-SCALE RESULTS AT THE BURGERSFORT WASTEWATER TREATMENT PLANT

4.2.1 Wastewater Treatment Works Performance

The following table 4-1 indicates the average basic chemical water quality of Burgersfort wastewater treatment works influent (raw sewage) and settling tank effluent that were applicable during the period of this study. The samples results were collected on monthly intervals from July 2011 to November 2013.

Table 4-1: The average basic chemical water quality of Burgersfort WWTWs influent and settling tank effluent for the studied period (July 2011 – November 2013).

Sample	Conductivity	pH	Nitrate	COD	Ammonia
General STD (DWAF, 1999)	***≤ 150 mS/m***	***5.5 -9.5***	***15mg/l***	***75mg/l***	***3mg/l***
Influent	96.90	7.36	2.30	207.00	0.20
Settled effluent	87.70	7.21	3.40	144.00	0.17

Table 4-2 illustrates the E. coli Count at Burgersfort wastewater works following the onsite application of chlorine at different dosage concentrations. Applied chlorine concentrations ranged between 7.50 and 8.50 mg/l for the period July to August 2011, between 5.00 and 12.9 for the period September 2011 to April 2012, between 3.80 and 6.90 mg/l for the period May to October

2012 and between 6.80 and 7.50 mg/l for the period November 2012 to March 2013. The mean and mode values of applied chlorine before mixing that were applied at the chlorine dosing point were 7.1 and 6.43 mg/l respectively. The data described above were collected before the installation of mixing apparatus at the point of chlorination the experimental set-up of mixing at the point of chlorination.

Table 4-2: E. coli Count and concentration of applied chlorine at Burgersfort wastewater works effluent disinfection during the period July 2011 to March 2013.

Date	E. coli (Count/100ml)			Applied Chlorine (mg/l)	
	STD	Median	Range	Mean	Range
July 2011 - Aug 2011	0	57.0	48 – 66	7.67	7.5 – 8.5
Sep 2011 - April 2012	0	2001	3 – 14450	7.70	5.00 - 12.9
May 2012 – Oct 2012	0	1500	10 - 67900	5.90	3.80 – 6.90
Nov 2012 – Mar 2013	0	272.5	64 - 2005	7.20	6.80 – 7.50

During the warm period between September 2011 and April 2012 chlorine dosages were higher than during the cold season. The warm season typically influences a higher application of chlorine at this specific plant since the dosing channel and contact tank are exposed to the outside environment. Exposure to the environment results in decreased disinfection which then leads to a need for increased chlorine dosage. However, the possibility of inadequate control and operation of the chlorination system could have contributed as well.

Table 4-3 illustrates the E. coli Count and concentration of the applied chlorine at the Burgersfort wastewater works after mixing was applied at the point of chlorination from April to November 2013. Applied chlorine concentration ranged from 3.0 to 7.5 mg/l, with a mean and mode value of 4.30 and 3.00 mg/l respectively. The chlorine dose requirement was significantly reduced by almost 50% compared to the dosage required when mixing was not applied (Table 4-2). It must be noted that, a zero (0) E. coli Count was achieved when mixing was applied on site (Table 4-3).

Table 4-3: E. coli Count and concentration of applied chlorine at Burgersfort wastewater works during the period April 2013 to November 2013 when mixing was applied.

Date	E. coli (Count/100ml)			Applied Chlorine (mg/l)	
	STD	Median	Range	Mean	Range
April 2013 – Nov. 2013	0	2.0	0.0 - 88	4.30	3.0 – 7.5

Table 4-4 shows the monthly effluent quality results obtained at the accredited laboratory for compliance monitoring requirements. The table shows the temperature and chlorine dosage, as well as E. coli Count and chlorine residual in the effluent at the Burgersfort WWTW for the period July 2011 to November 2013. Mean concentration of chlorine residual discharged into the environmet shows a reduction of over 80% (that is; 0.57 mg/l and 0.081 mg/l before and after mixing respectively). The results also show that the chlorine dosage and E. coli inactivation were significantly reduced and improved (40% and 95%) respectively when mixing was applied at the chlorination sump on site. This was achieved irrespective of the impact of other common factors that influence the action of disinfectants. The dosage of chlorine after mixing was implemented even below the mean determined chlorine demand of 6.5 mg/l (Figure 4-6).

Table 4-4: Monthly monitored effluent quality data for the Burgersfort Wastewater Works.

DATE	Temperature	E. coli	Cl_2 residual	Cl_2 dosed	Comment
2011/07/12	12	48	*	8.0	**BEFORE MIXING**
2011/08/10	19	66	1.2	8.0	
2011/09/06	18	201	*	6.1	
2011/10/11	24	2001	*	6.4	
2011/10/25	25	2001	*	5.4	
2011/11/08	21	14450	*	5.9	
2011/11/22	22	4400	0.33	10.4	
2011/12/13	21	62	0.56	12.9	
2011/12/20	24	3	0.5	6.4	
2012/01/11	22	201	*	10.3	
2012/01/24	22	10900	*	5.0	
2012/02/14	19	624	*	7.3	
2012/03/13	21	4780	0.6	7.7	
2012/03/27	20	2220	0.46	8.7	
2012/04/10	18	530	0.55	7.4	
2012/05/08	16	238	*	6.4	
2012/05/30	18	4530	0.5	6.6	
2012/06/12	14	1500	0.55	5.7	
2012/07/11	16	100	0.65	6.1	
2012/08/02	15	67900	*	3.8	
2012/08/28	16	2380	*	6.6	
2012/09/25	19	74	0.82	6.9	
2012/10/09	22	20050	0.55	5.3	
2012/10/30	21	10	0.47	5.7	
2012/11/27	24	344	0.55	7.0	
2012/12/11	21	64	*	7.4	
2012/12/18	26	2005	0.75	6.8	
2013/01/15	25	384	0.6	7.5	
2013/01/29	24	201	*	7.2	
2013/02/12	20	87	*	7.2	
2013/03/09	26	88	0.02	7.4	
2013/03/26	23	0	0.05	7.5	
2013/04/16	21	34	0	5.1	**AFTER MIXING**
2013/05/14	18	2	0.02	4.0	
2013/06/11	19	0	0.11	3.5	
2013/07/09	20	0	0.16	3.2	
2013/08/13	22	5	0.1	3.0	
2013/09/10	19	0	0.2	3.1	
2013/10/08	23	13	0.03	3.0	
2013/11/12	25	2	0.06	3.0	
Median and Mean reading Before Mixing		**1500**	**0.57**	**7.12**	
Median and Mean reading After Mixing		**2.0**	**0.0081**	**4.30**	

***** *No reading taken*

Figure 4-1 illustrates the trends in monthly monitored effluent quality at the Burgersfort Wastewater Works. E. coli Count/100ml during the period under study ranged from 254 and >20050 Count/100ml. E. coli was present in the effluent samples taken from July 2011 to March 2013 after chlorination, while from April 2013 zero(0) E. coli Count were often observed.

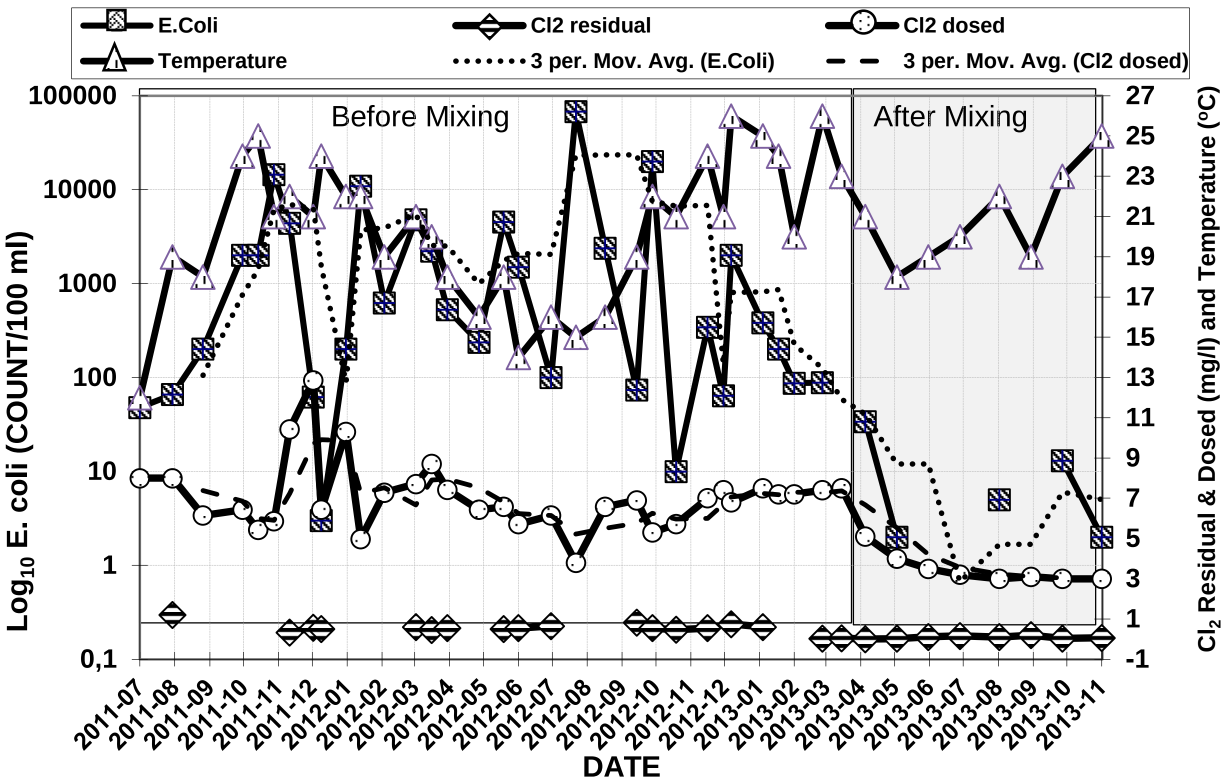

Figure 4-1: Monthly monitored effluent quality trend of Burgersfort Wastewater Works.

4.2.2 Typical chlorine demand curve of Burgersfort WWTW secondary effluent.

The chlorine demand test carried out randomly for Burgersfort WWTW samples during the period of July 2011 to November 2013 indicates that break point chlorination was on average of 6.5 mg/l (Figure 4-2).

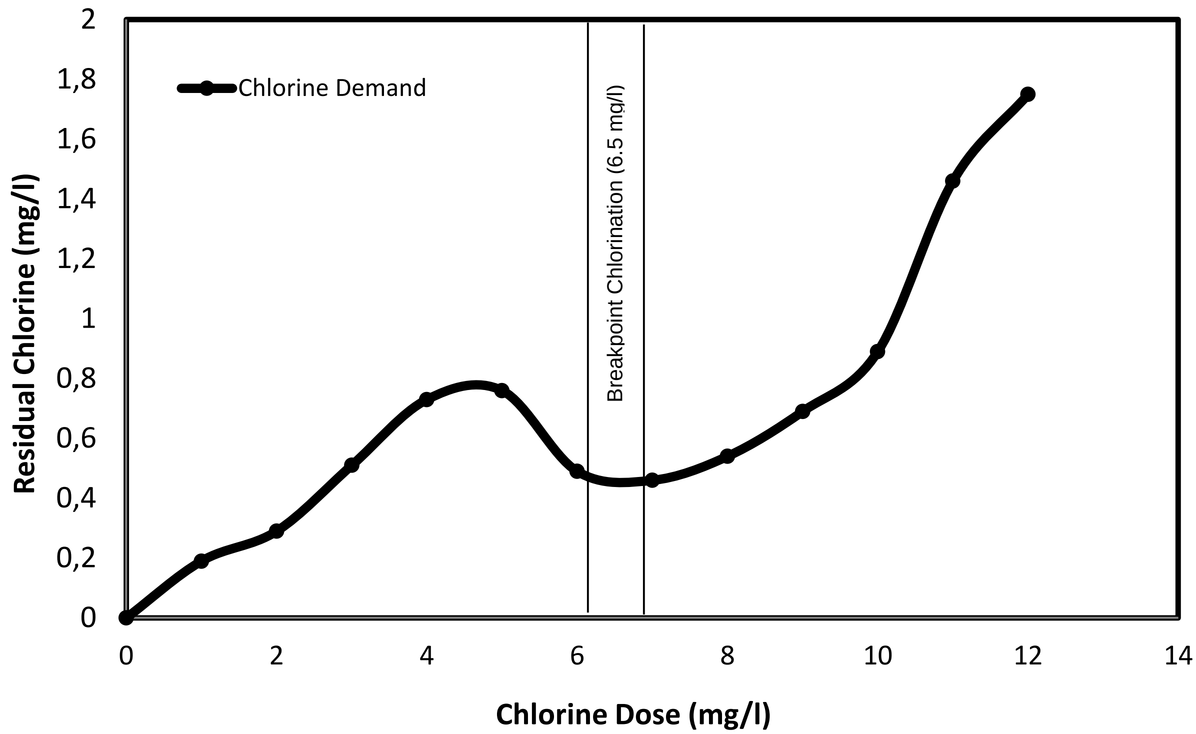

Figure 4-2: Typical chlorine demand curve at the Burgersfort WWTW secondary effluent (chlorine demand between 6-7 mg/l).

4.2.3 Correlations between Chlorine Demand and Other Determinants.

A regression analysis was done with subscales of water quality parameters, such as temperature, COD, ammonia nitrogen, and suspended solids/turbidity as independent variables and the subscale of chlorine demand as dependent variable. Regression analysis provides estimates of the mean amount by which a dependent variable changes when there is a change by one unit or the other of an independent variable. A mathematical equation was generated that exhibit how the variation in chlorine demand can be explained by the variation in each of the water quality parameters listed above, that is; temperature, COD, ammonia nitrogen and suspended solids/turbidity.

An important output of regression analysis is the multiple correlation coefficient, R^2, which indicates how well data fit a statistical model. The accuracy of an estimate of this nature depends on the extent to which the regression equation actually fit the data, and the accuracy of the regression line depends on the degree of scatter in the data.

The following results were analysed to establish the relationship between chlorine demand and temperature, COD, ammonia nitrogen and suspended solids/turbidity respectively. The analysis was performed on onsite chlorine demand tests on effluent sampled at the Burgersfort Wastewater Treatment Works over the period of July 2011 to February 2013:

Figure 4-3 shows a fair positive correlation between temperature and chlorine demand, that is; that only a 30.8 percent (that is; $R^2 = 0.3079$) variation in chlorine demand can be explained by temperature.

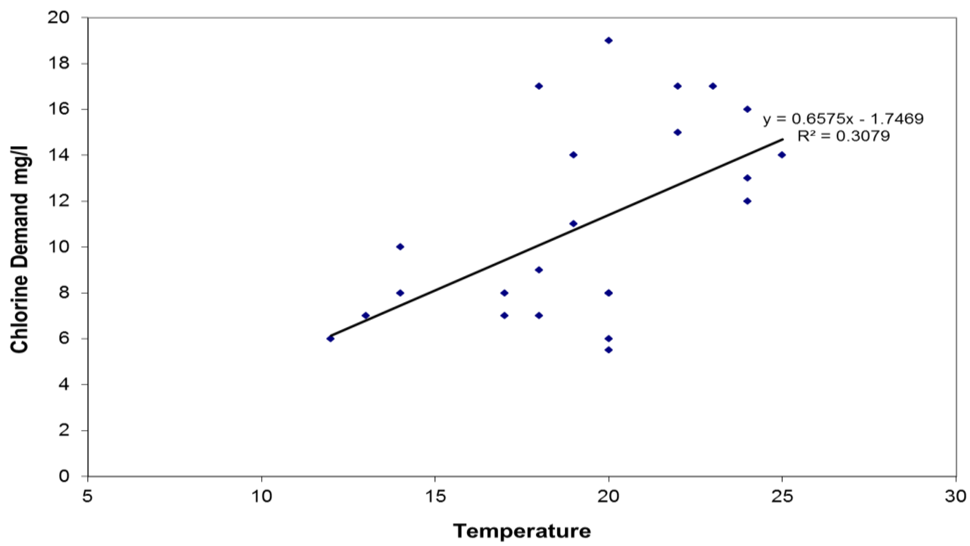

Figure 4-3: Correlation for Burgersfort WWTW effluent quality with temperature as independent variable and Chlorine demand as dependent variable.

In Figure 4-4, the results show a significant degree of scatter in the data and a weak positive correlation between COD concentration in the effluent and chlorine demand that is only a 21 percent variation in chlorine demand can be explained by the COD concentration in the effluent.

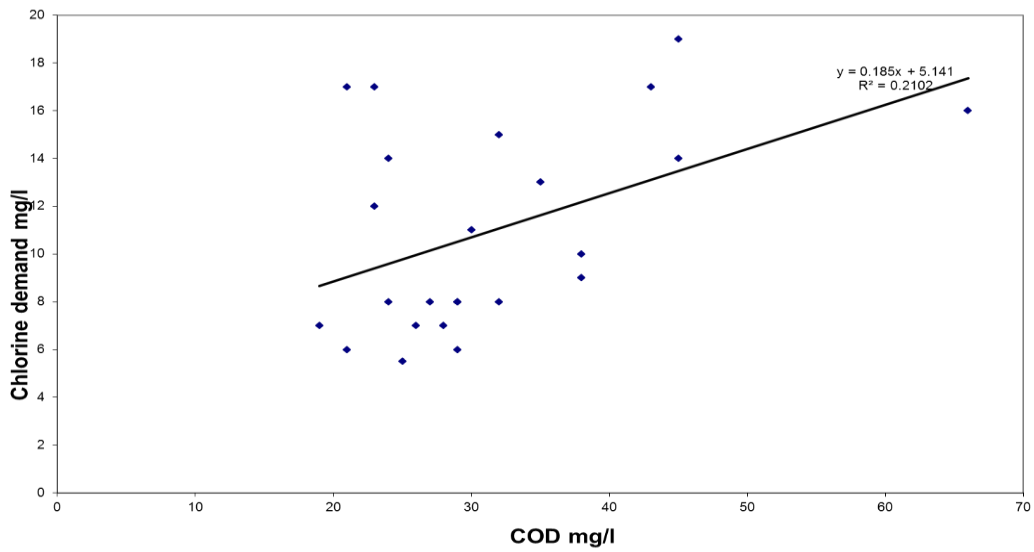

Figure 4-4: Correlation for Burgersfort WWTW effluent quality with COD as independent variable and Chlorine demand as dependent variable.

In Figure 4-5, the results show a significant degree of scatter in the data and a weak negative correlation between ammonia nitrogen concentration in the effluent and chlorine demand that is an 18.3 percent variation in chlorine demand can be explained by the ammonia nitrogen concentration in the effluent.

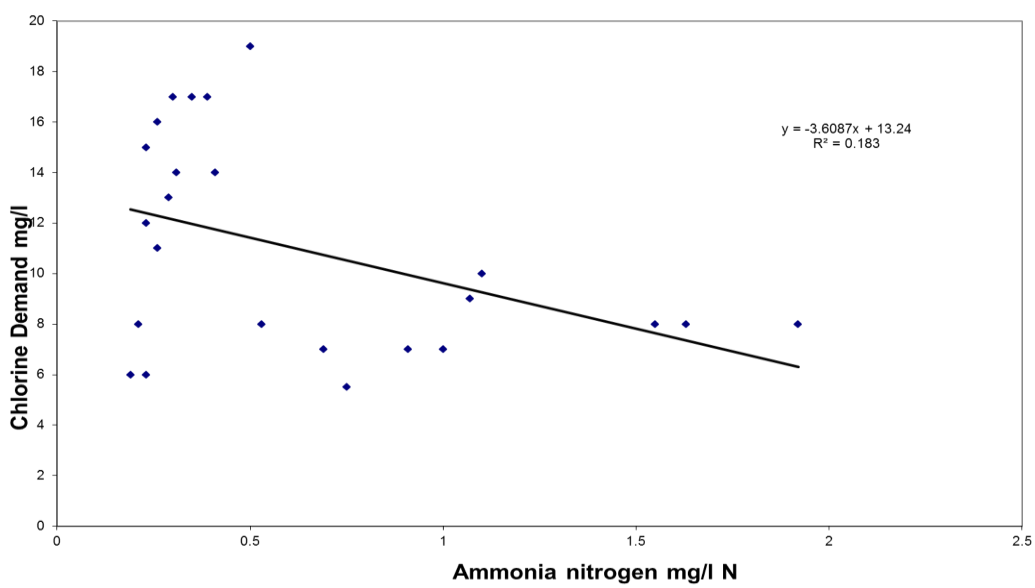

Figure 4-5: Correlation for Burgersfort WWTW effluent quality with ammonia nitrogen as independent variable and chlorine demand as dependent variable.

Figure 4-6 shows a higher degree of scatter in the data as compared to the other determinants tested (temperature, COD, ammonia nitrogen). The results also show a very weak positive correlation between suspended solids and chlorine demand that is only a 2.8 percent variation in chlorine demand can be explained by the concentration of suspended solids in the effluent.

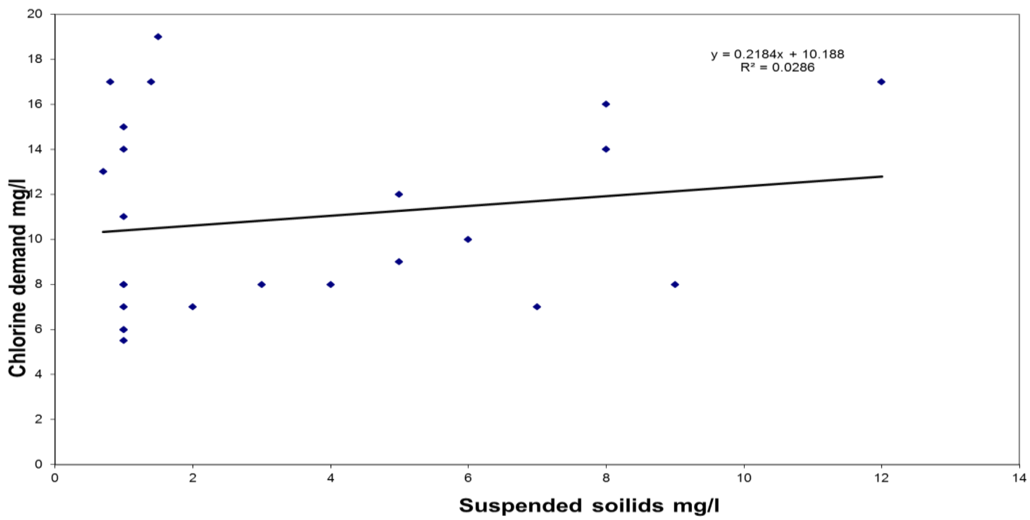

Figure 4-6: Correlation for Burgersfort WWTW effluent quality with suspended solids as independent variable and chlorine demand as dependent variable.

4.2.4 Study Correlations of Chlorine Dosed and E. coli inactivation

Figure 4-7 shows a goog correlation between chlorine dosed and E. coli in the effluent, that is 55.8 percent (that is; $R^2 = 0.558$) variation in E. coli inactivation can be explained by Chlorine dosed.

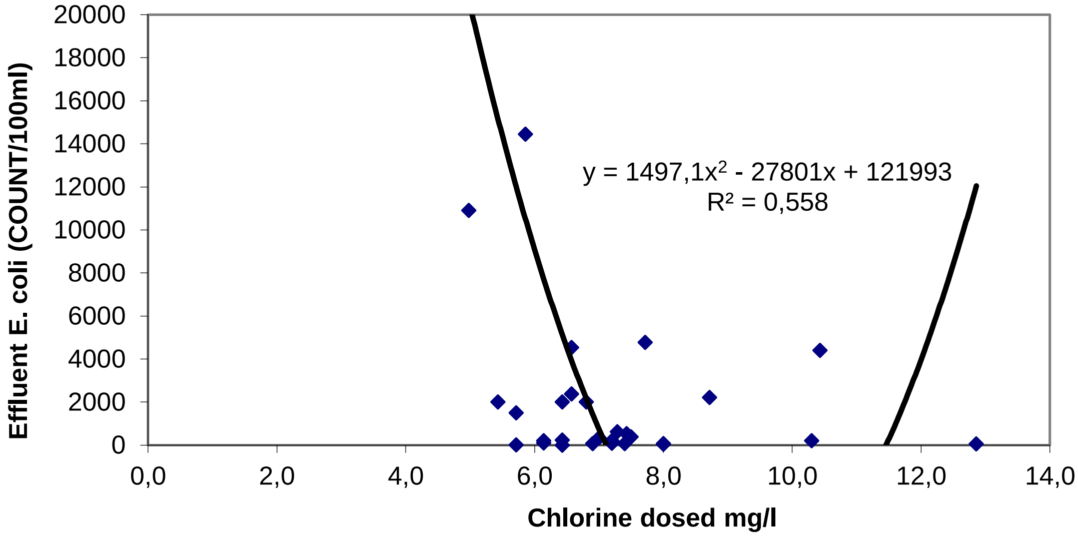

Figure 4-7: Correlation for Burgersfort WWTW effluent quality with chlorine dosed as independent variable and E. coli as dependent variable.

4.3 LABORATORY INVESTIGATIONS: BURGERSFORT WASTEWATER TREATMENT PLANT

This laboratory batch scale experiment was aimed at determining ways of improving the microorganism inactivation at a dosage concentration less than the chlorine demand and to establish factors affecting the optimisation of chlorine disinfection.

4.3.1 Chlorine demand experiments

Table 4-5 and Figure 4-8, 4-9 and 4-10) show the chlorine demand experiments carried out in triplicate for the same sample when performing these experiments indicates that break point chlorination was in the range of 6-7 mg/l.

Table 4-5: Chlorine demand data at the Burgersfort WWTW secondary effluent

Chlorine Dose (mg/l)	Chlorine residual (mg/l)		
	Test 1	Test 2	Test 3
0	0	0	0
1	0,19	0,05	0,12
2	0,29	0,26	0,21
3	0,51	0,6	0,39
4	0,73	0,68	0,71
5	0,76	0,8	0,78
6	0,49	0,44	0,52
7	0,46	0,43	0,41
8	0,54	0,47	0,45
9	0,69	0,65	0,75
10	0,89	0,69	0,88
11	1,46	0,98	1,03
12	1,75	1,45	0,87

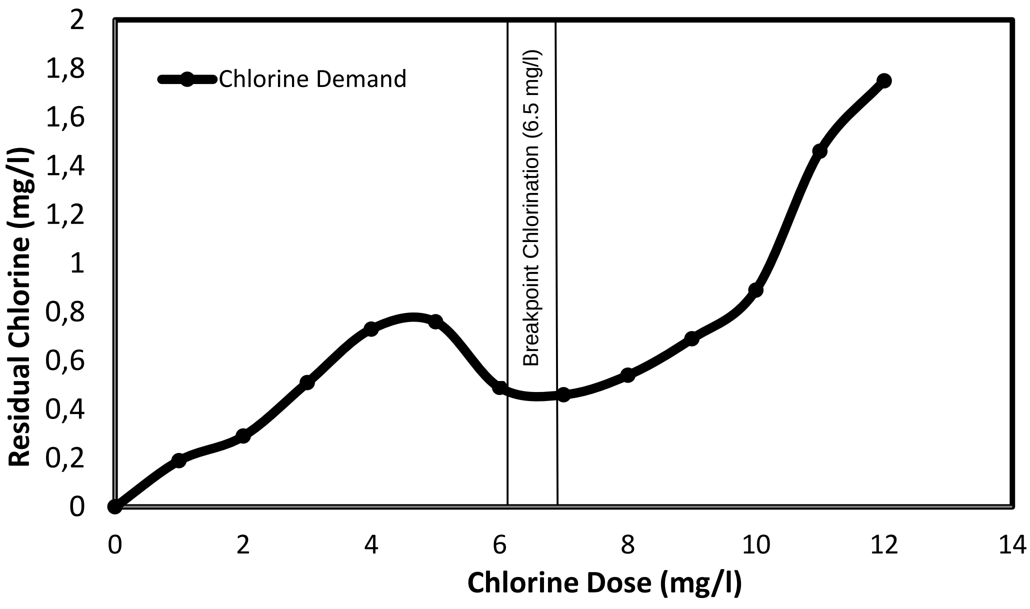

Figure 4-8: Test 1 chlorine demand curve at the Burgersfort WWTW secondary effluent (chlorine demand of 6.5 mg/l).

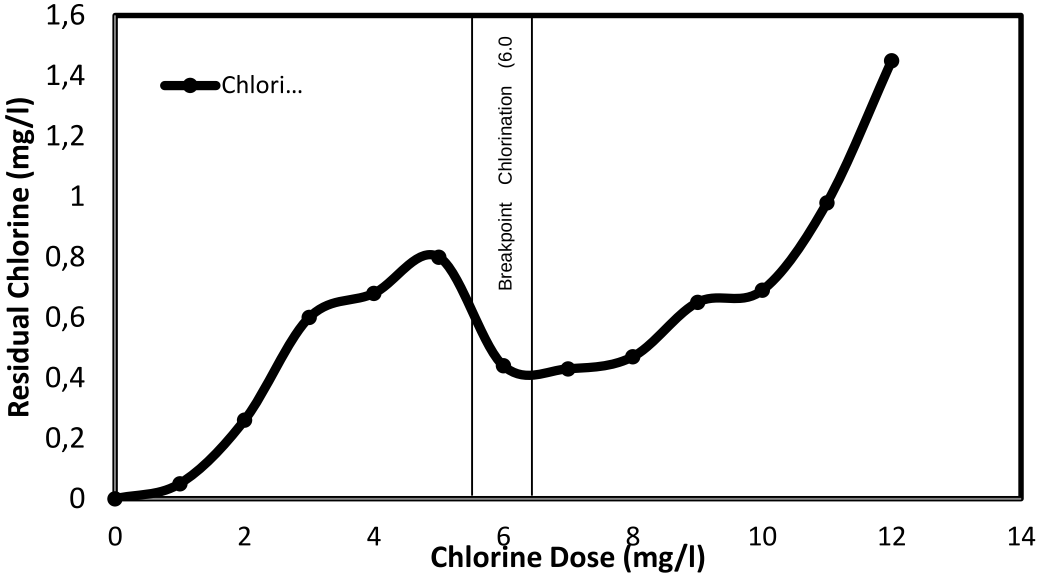

Figure 4-9: Test 2 chlorine demand curve at the Burgersfort WWTW secondary effluent (chlorine demand of 6.0 mg/l).

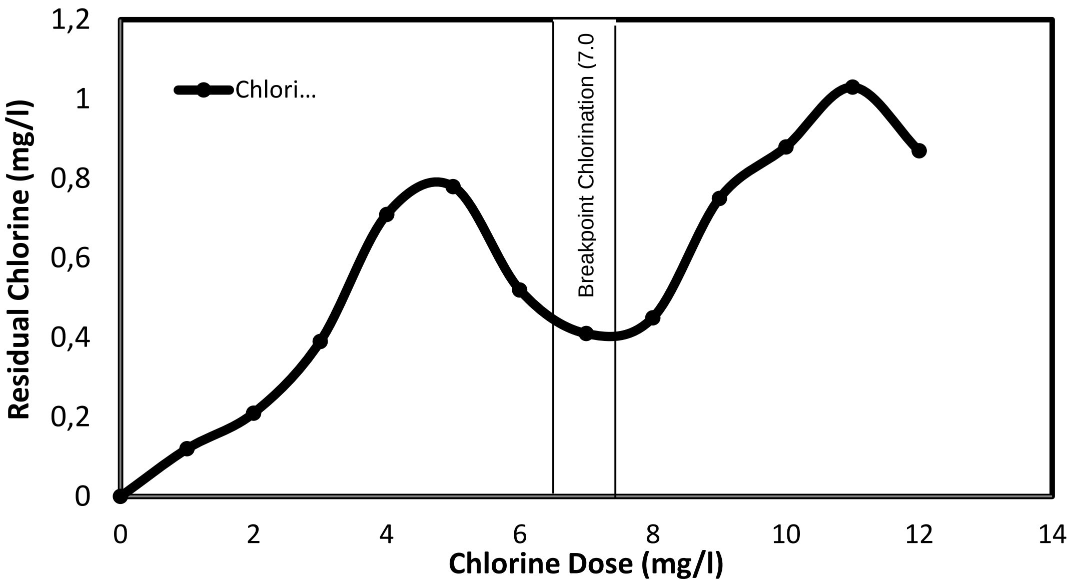

Figure 4-10: Test 3 chlorine demand curve of Burgersfort WWTW secondary effluent (chlorine demand of 7.0 mg/l).

4.3.2 The effect of increased substance concentration and contact time on E. coli inactivation

Table 4-6 shows the results illustration that sufficient sufficient inactivation of E. coli was achieved prior to spiking the secondary effluent from the humus/settling tank with raw sewage in order to measure the effect of increased substance/pollutant concentration on E. coli inactivation. Table 4-5 also illustrates that Total chlorine was only available after a contact time of 60 minutes.

The pH of 7.33 contributed to achieving optimal conditions for disinfection. At this pH hypochlorous acid (HOCl) is formed and at a neutral level, it has a greater ability to penetrate and kill the negatively charged organisms.

Table 4-6: Mean inactivation of E. coli prior to spiking of the secondary effluent from humus tank.

Determinates	0 mg/l Cl2 dosed	3mg/l chlorine concentration dosed			Number of reading mean
		15 min.	30 min.	60 min.	
pH	7.33	7.37	7.33	7.3	4
Turbidity (NTU)	5.3	6.4	2.75	2.45	4
Nitrate mg/l N	48	51	55	45	4
Nitrite mg/l N	0.9	0.03	0.03	0.03	4
COD mg/l	24	26	33	32	4
Ammonia N	0.42	0.7	0.68	0.41	4
E. coli (Count/100)	1733	2	0	0	4
Free Cl_2 mg/l	0	0	0	0	4
Total Cl_2 mg/l	-	-	-	0.7	4

- = Not done

Tables 4-7 and 4-8 show the results obtained when adding 3 mg/l chlorine to samples from humus tank effluent spiked with raw water. Although the pH did not exceed 7.5 and optimal conditions for disinfection were achieved, results indicated that the increased substance/pollutant concentrations impacted negatively on disinfection efficacy. Thus, suspended solids (SS) adsorb the targeted microbials and shield them from contact with the disinfectant (Le & Zhang, 2013; Metcal & Eddy, 1991; 2004).

Table 4-7: The effect of increased substance/pollutant concentration on E. coli inactivation in samples spiked with raw sewage (influent) at a 1:7 (Influent: humus tank effluent) ratio; chlorine dosed at 3mg/l

Determinates	0 mg/l Cl2 dosed	3 mg/l chlorine concentration dosed			Number of reading mean
		15 min.	30 min.	60 min.	
pH	7.44	7.45	7.51	7.27	4
Turbidity (NTU)	7.87	15.4	21.2	18.2	4
Nitrate mg/l N	34	38	40	40	4
Nitrite mg/l N	3	1	0.03	0.03	4
COD mg/l	-	80	59	96	4
Ammonia N mg/l	11	11.4	11.2	11.25	4
E. coli (Count/100)	>2420	4	0	6	4
Free Cl_2 mg/l	0	0	0	0	4
Total Cl_2 mg/l	-	-	-	0.45	4

- = Not done

Table 4-8: The effect of increased substance/pollutant concentration on E. coli inactivation in samples spiked with raw sewage (influent) at a 1:3 (Influent: humus tank effluent) ratio; chlorine dosed at 3mg/l

Determinates	0 mg/l Cl2 dosed	3 mg/l chlorine concentration dosed			Number of reading mean
		15 min.	30 min.	60 min.	
pH	7.45	7.53	7.43	7.4	4
Turbidity (NTU)	24.9	34.1	32.2	34.1	4
Nitrate mg/l N	16	22	22	30	4
Nitrite mg/l N	8.8	7.5	7.5	2.8	4
COD mg/l	-	134	140	140	4
Ammonia N mg/l	22.5	23.75	24.3	23.75	4
E. coli (Count/100)	>2420	8	2	5	4
Free Cl_2 mg/l	0	0	0	0	4
Total Cl_2 mg/l	-	-	-	0.04	4

- = Not done

As shown when comparing Tables 4-6, 5-7 and 4-8, the concentration of various substances/pollutants increased with the addition of raw water. It is expected that the chlorine demand would also increase and that a higher chlorine dose would be required to achieve the same results had this increase not occurred. The effect of increased contact time under these circumstances was found to be negligible as total chlorine was evident after 60 minutes of chlorine dosage irrespective of the degree of pollution. As can be seen in the E. coli count after 60 minutes of disinfection in Table 4-7 and Table 4-8.the detection of E. coli after 30 minutes of disinfection could be due to one or a combination of the following factors:

- Increased suspended solids (turbidity) shielding bacteria (E. coli) and thus less effective disinfection;

- Increased nitrite concentration after spiking and thus an increased chlorine demand needed to oxidize the nitrite into nitrate (see Equation 4-1). This is also indicated by the decrease in nitrites and increase in nitrates after chlorination (Tables 4-7 and 4-8):

  Nitrite was oxidised to nitrate by chlorine.

  $$\mathbf{NO_2^- + H_2O + Cl_2 \rightarrow NO3^- + 2HCl} \qquad \mathbf{4\text{-}1}$$

  With the increased chlorine demand, there was likely less chlorine for disinfection.

- The number of organisms present also increased with spiking. Although the concentration of organisms is seldom a major consideration, longer contact times are required for larger organism concentrations.

- The inactivation rates of indicator organisms in sample prior to spiking of the secondary effluents were markedly similar to those found in secondary effluent samples spiked with raw sewage (Influent). Table 4-7 and 4-8 show that the optimum contact time for inactivation is at 30 minutes contact time. The E. coli counts show increase at 60 minutes contact time and this could be due to shielding effect on microorganism by suspended solids in the water, in which microorganism started to move out of lasting shields and/or microorganism clumps as contact time increases beyond 30 minutes.

i. Macauley *et al*. (2006) in their study of disinfection of swine wastewater using chlorine found that bacteria inactivation was slightly more effective in the centrifuge sample than in the raw sample. This indicates that the suspended solids did inhibit bacteria inactivation, but the inhibition was not significant.

ii. Li and Zhang (2013) in their study found that inactivation behaviours of the target antibiotics under ammonia nitrogen concentrations ranging from 2 to 15 mg/l were characterised by a rapid initial inactivation rate on contact with free chlorine during the first 5 seconds to 1 minute (depending on the specific antibiotic and ammonia nitrogen concentration) and then a much slower inactivation rate. Free chlorine was responsible for the reaction with antibiotics during the rapid stage (first 5 sec. to 1 min.), whereas combined chlorine reacted with antibiotics in the subsequent slow stage.

4.3.3 The effect of increased contact time and increased dosing concentration on E. coli inactivation

Table 4-9 shows the effect of increased dosage concentrations and increased contact time (CT value) on E. coli inactivation efficiency. Depending on the concentration of residual chlorine, microorganisms that were not in contact with (or exposed to) chlorine during dosing would be deactivated by the available chlorine residual during increased contact time**.** The chlorine demand carried out in triplicate for the same sample when performing these experiments was found to be in the range of 6-7 mg/l.

The maximum HRT to achieve complete inactivation of E. coli is 2.5 min, corresponding with the initial E. coli concentration of 108 Count/100 ml (Nanayakkara *et al*., 2012).

Table 4-9: Effect of increased chlorine dosing concentration and contact time (CT value) on E. coli inactivation.

Determinates	Humus Tank	2mg/l [Cl2] dosed		4mg/l [Cl2] dosed		6mg/l [Cl2] dosed		Number of reading mean
		20 min.	40 min.	20 min.	40 min.	20 min.	40 min.	
pH	7.16	7.14	7.13	7.11	6.98	7	6.93	5
Nitrite mg/l N	0.56	0.34	0.33	0.10	0.03	0.03	0.03	5
E. coli (Count/100)	>2420	411	16	4	0	0	0	5
Free Chlorine	-	0	0	0	0	0.03	0.01	5
Total Chlorine	-	0.22	0.20	0.38	0.56	0.74	0.71	5

- = Not done

Because hypochlorous acid is very active oxidizing agent, it reacts readily with ammonia in the wastewater to form three types of chloramines in the successive reaction depending on the pH, temperature, contact time and ratio of chlorine to ammonia. With higher concentrations of ammonia present after spiking, chloramines are probably formed. If the ammonia-N concentration in the effluent is greater than the nitrite-N concentration, which was the case in the samples analysed, the residual will probably form monochloramine and be stable (Phoenix 1995). The formation of chloramines, which are more effective over longer periods of time, could also have contributed to the further inacativation rates obtained with increased contact times. Ammonia plays a critical role during chlorination because of its competition with antibiotics for free chlorine to form combined chlorine, which reacts slowly with these antibiotics (Li & Zhang, 2013).

For all sets of initial conditions, chlorine demand increases with increasing contact time and approaches a constant value, the ultimate chlorine demand (Helbling & Van Briesen, 2007).

4.3.4 The effect of mixing on E. coli inactivation

Table 4-10 and 4-11 shows the effect of mixing on the inactivation of E. coli bacteria. The table shows that contact time is important for E. coli inactivation where no mixing is applied. The results show a relationship between the mixing (no mixing, gently mixing and vigorous mixed), dosing concentration and contact time. It would thus be possible for operational staff at the treatment works to determine a cost-effective application for specific circumstances. During mixing, chlorine is consumed by nitrite and ammonia while simultaneously inactivating (killing) microorganisms and lower chlorine concentrations are consequently required. This shows that mixing increases the exposure of microorganisms to free chlorine before it reacts with disinfection competing organics and chemicals in the effluent, which results in the inactivation of bacteria at relatively low chlorine doses. This finding is contrary to the finding by Jeong *et al*. (2006) who reported a reduction in the disinfection efficiency with an increase in the initial population of E. coli in the electrochemical inactivation of E. coli in KH_2PO_4. Their study suggests that the consumption of oxidants is higher if the initial concentration of bacteria was high. They concluded that the chlorine produced is consumed by the microorganisms, while this study shows that inactivation of microorganisms depends on the microorganism's exposure and/or contact with chlorine and is independent of the initial concentration of microorganism and chlorine. Le and Zhang (2013) also found a rapid initial inactivation rate of antibiotics upon contact with free chlorine. The free chlorine was responsible for the reaction with antibiotics during the rapid stage (first 5 sec - 1 min), whereas combined chlorine reacted with antibiotics in the subsequent slow stage.

Table 4-10 shows the results of the effect of mixing, contact time and chlorine concentration on actual detected E. coli concentration inactivated and residual E. coli concentration after inactivation.

Table 4-10: Effect of mixing, contact time and chlorine concentration on E. coli Inactivation

Dosed Cl_2 Concentrations	**E. Coli Concentration (Count/100ml)**									**Number of reading mean (Observation)**
	No mixing			Gently Mixed (low intensity)			Vigorously Mixed (high intensity)			
	1min	2min	3min	1min.	2min.	3min.	1min.	2min.	3min.	
0 mg/l	2420	2420	2420	2420	2420	2420	2420	2420	2420	2
1 mg/l	812	600	641	493	496	493	25	16	16	4
2 mg/l	520	411	399	20	24	11	4	0	2	4
3 mg/l	603	364	320	8	4	4	0	0	0	4
4 mg/l	431	294	111	6	2	4	2	0	0	4
5 mg/l	387	200	89	2	2	0	0	0	0	4

Table 4-11 shows the results of the effect of mixing, contact time and chlorine concentration on Log_{10} E. coli inactivation and free residual chlorine. Free residual chlorine was only detected in the samples where no mixing of chlorine dosed with effluent was applied. In a no-mixing system, free residual chlorine increased from 0 mg/l to 0.21 mg/l respectively as chlorine doses were increased from 0 mg/l to 5 mg/l. However, as the contact time increased from one minute to 3 minutes the free residual chlorine also proportionately reduced.

Table 4-11: Effect of mixing, contact time and chlorine concentration on Log10 E. coli inactivation.

Dose $[Cl_2]$	Mixing intensity and contact time																		Number of reading mean (Observation)
	No mixing						Gently mixed (low intensity)						Vigorously mixed (high intensity)						
	1min		2min		3min		1min.		2min.		3min.		1min.		2min.		3min.		
	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	Log_{10} E. coli (Count/100ml)	Free Cl_2 (mg/l)	
0 mg/l	3.38	0	3.38	0	3.38	0	3.38	0	3.38	0	3.38	0	3.38	0	3.38	0	3.38	0	2
1 mg/l	2.91	0	2.78	0	2.81	0	2.69	0	2.70	0	2.69	0	1.40	0	1.20	0	1.20	0	4
2 mg/l	2.72	0.1	2.61	0	2.60	0	1.30	0	1.38	0	1.04	0	0.60	0	#	0	2.00	0	4
3 mg/l	2.78	0.03	2.56	0.03	2.51	0.02	0.90	0	0.60	0	0.60	0	#	0	#	0	#	0	4
4 mg/l	2.63	0.13	2.47	0.09	2.05	0.08	0.78	0	0.30	0	0.60	0	0.30	0	#	0	#	0	4
5 mg/l	2.59	0.21	2.30	0.23	1.95	0.09	0.30	0	0.30	0	#	0	#	0	#	0	#	0	4

Figure 4-11, 4-12 and 4-13 show the effect of applying mixing on E. coli inactivation during chlorine disinfection. The results indicate that when mixing is applied and the mixing is applied vigorously, inactivation of E. coli as indicator bacteria to 0 Count/100ml can be achieved at a significant reduced chlorine dose as compared to the chlorination system where mixing is not applied. The high inactivation rate was obtained during the first minute of contact time, which could be due to the presence of free chlorine residual quickly exposed to E. coli bacteria by mixing before it has reacted with other chlorine demanding substances in the effluent. No significant changes were observed on E. coli inactivation as the contact time increased from one minute to two and three minutes respectively.

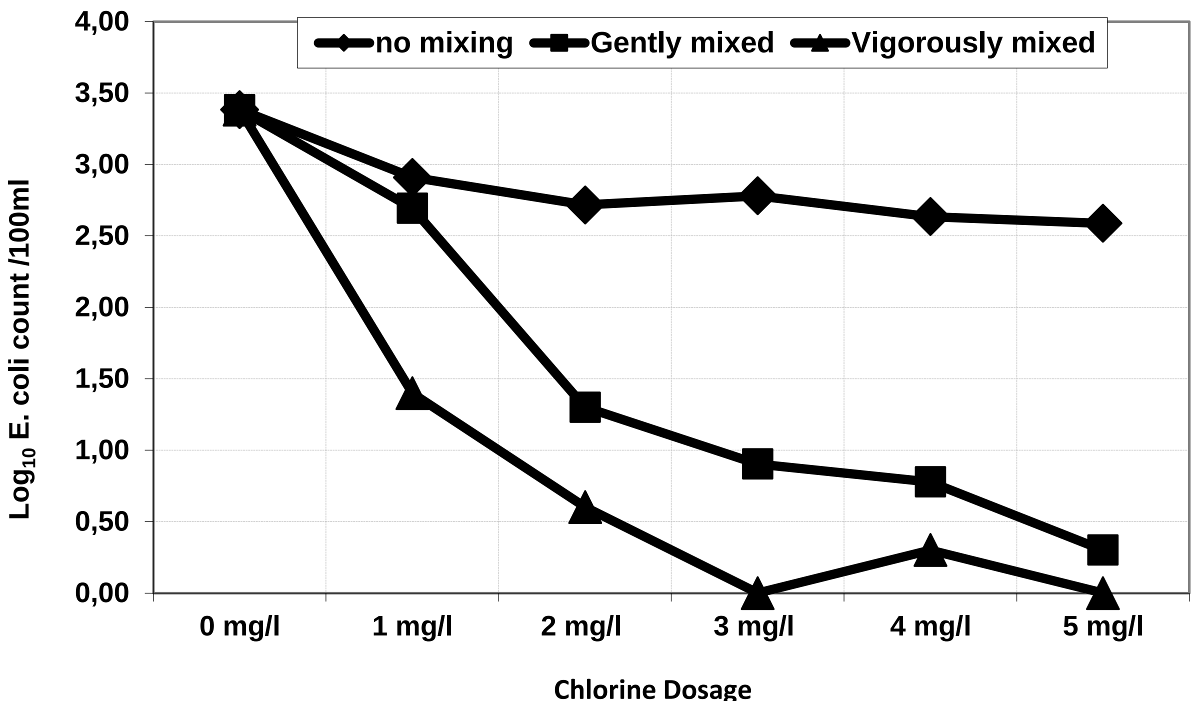

Figure 4-11: Effect of mixing after 1 minute of contact time

The following shows Linear Equation and R-squared value for Figure 4-11.

No mixing:
Y = -0.1355x + 3.3095 **4-2**
R^2 = 0.7552

Gently Mixed:
y = -0.6159x + 3.7156 **4-3**
R^2 = 0.9087

Vigorously Mixed:
y = -0.5946x + 3.0287 **4-4**
R^2 = 0.7304

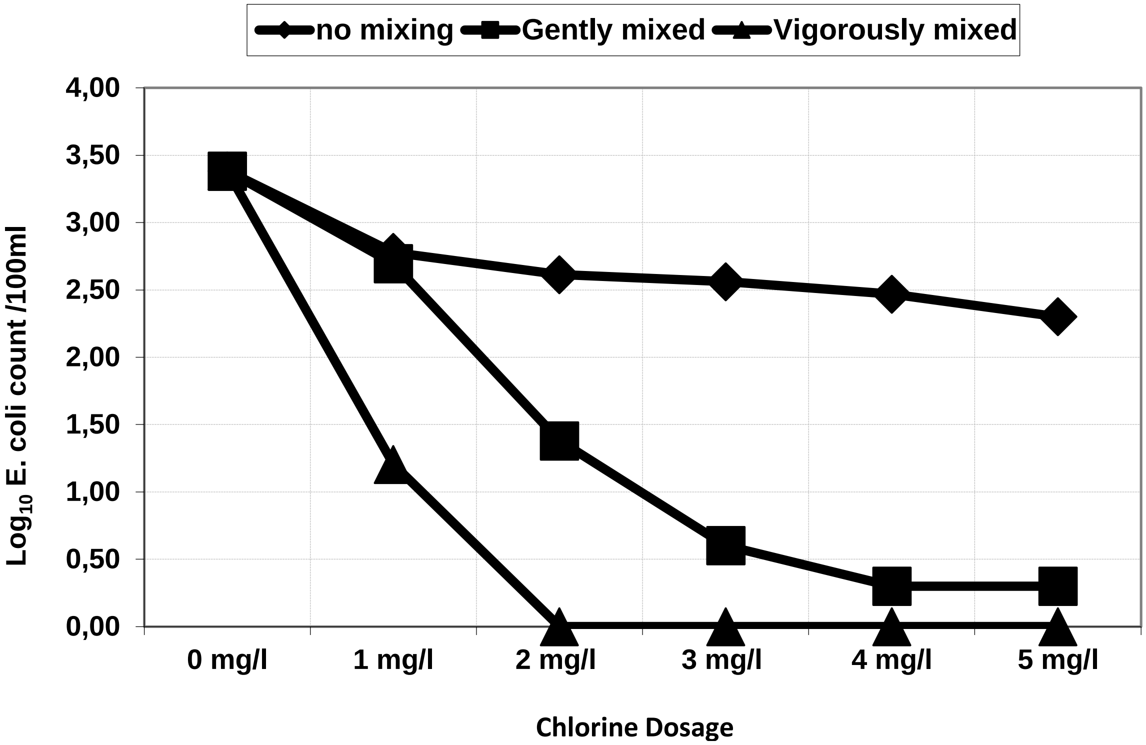

Figure 4-12: Effect of mixing after 2 minutes of contact time

The following shows Linear Equation and R-squared value (Figure 4-12)

No mixing:
y = -0.1827x + 3.324 **4-5**
R^2 = 0.821

Gently Mixed:
y = -0.6679x + 3.7815 **4-6**
R^2 = 0.9019

Vigorously Mixed:
y = -0.5866x + 2.8178 **4-7**
R^2 = 0.6412

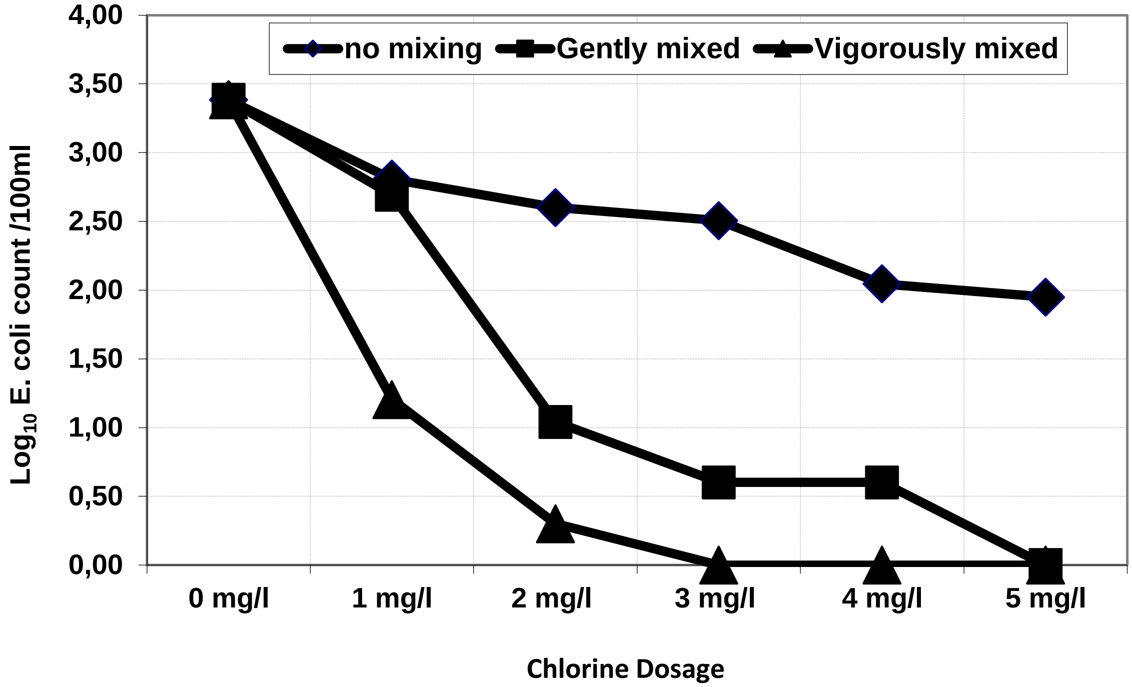

Figure 4-13: Effect of mixing after 3 minutes of contact time

The following shows Linear Equation and R-squared value (Figure 4-13)

No mixing:
$y = -0.2729x + 3.5038$ **4-8**
$R^2 = 0.9438$

Gently Mixed:
$y = -0.6752x + 3.7501$ **4-9**
$R^2 = 0.8895$

Vigorously Mixed:
$y = -0.5952x + 2.8981$ **4-10**
$R^2 = 0.6883$

4.4 DISCUSSION

In the batch experiments, the free chlorine concentration was generally observed to undergo two phases of decay consisting of an initial phase of relatively fast decay kinetics, followed by slower decomposition (Page *et al*, 2009). However, most wastewater treatment plants employing chlorination add the chlorine as an aqueous solution through a diffuser at the head of a chlorine contact basin with little or no effective mixing. Before the chlorine stream is thoroughly mixed with the mass of incoming wastewater under these transport conditions, reactions competing with the disinfection process result in the formation of chloramines, other by-products and a rapid depletion of free chlorine (Longley, 1978).

Tables 4-10 and 4-11 showed that inactivation occur at two rates, an initial rapid kill followed by a slower kill. For each applied chlorine dose, the highest inactivation rate was obtained during the first one minute of contact time, which could be due to the presence of free chlorine residual that had not yet reacted with chlorine demanding substances. The subsequent slower kill can possibly be attributed to the formation of less potent combined chlorine residual as a result of reactions between free chlorine residual and chlorine demanding substances (mainly NH_3).

Mixing, in this study, has been proven to be another important factor for chlorine disinfection among those that are well documented to date (including contact time, concentration and type of chemical agent, intensity and nature of physical agent, pH, temperature, number of organisms, type of organisms, age of the organisms, nature of suspending liquid and chlorine demand). The importance of mixing was also put in proper perspective in the study by Longley (1978). This study revealed that rapid mixing of chlorine with wastewater may achieve the required degree of disinfection by using less chlorine, and this will result in significant savings in chlorine dosing. This proposition was confirmed in this study by tests conducted in a full-scale investigation (Table 4-4), where the chlorine dosage required to inactivate E. coli at the Burgersfort WWTW effluent was reduced by 50% (from mean of 7.12 mg/l before mixing to a mean of 4.30 mg/l after mixing).

There are mixing devices that should ideally be able to homogenise the chlorine solution and wastewater in a fraction of a second. Mixing has the advantage of quickly dispersing the chlorine solution, which provides optimum utilisation of the disinfectant in a turbulent regime (White, 1999).

Mixing in chlorine disinfection practice will also reduce the free and combined chlorine residual discharged into water resources. One of the current disadvantages of using chlorine as a disinfectant is chlorine residual that is discharged into water courses and which becomes toxic to aquatic organisms. The available residual chlorine also has the potential to form organo-chlorinated derivatives. These derivates are of particular concern, as they tend to be relatively toxic, persistent and bio-accumulative.

CHAPTER 5

5 CONCLUSIONS

5.1 CONCLUSIONS OF THIS STUDY

The results of this study provide clear evidence that there is a significant opportunity to meet standardised E. coli limits for discharging effluent into a water course when reduced chlorine dosage is applied with mixing.

The rate at which E. coli is inactivated is affected by the application of mixing chlorine with the wastewater effluent at the point of dosage during the chlorination process. The higher the intensity of mixing, the less chlorine is required. However, the impact is significant at lower dosing concentrations. In this study, dosing concentration were 1, 2, 3, 4 and 5 mg/l and the significant effect was shown at dosage between 2-3 mg/l. Higher dosing concentrations may compensate for lower turbulent/mixing at the dosing point. It could thus be concluded that the inactivation of E. coli as an indicator bacterium is enhanced by increased mixing energy at the point of dosing. The mixing provides initial disinfection by providing for the free residual chlorine to diffuse into the microorganism clumps, causing a rapid kill during the initial contact period. Therefore, bacteria inactivation is quantified as a function of disinfectant exposure (see Figure 4-11, 4-12 and 4-13). The benefit of this finding is that it would be possible to achieve the wastewater standard for E. coli at a dosing concentration less than what is required for breakpoint chlorination. Longley (1978) reports on a survey of the chlorination facilities of several wastewater treatment plants discharging into San Francisco Bay and found that plants introducing chlorine at a point of turbulence demonstrated consistently higher coliforms inactivation.

Adequate wastewater treatment is important to protect the environment to which wastewater is discharged into. In the design of chlorine contact tanks, the principle concern must be to achieve maximum disinfection efficiency with a minimum chlorine residual. The current conventional methods of chlorine addition do not take advantage of the short time that free chlorine is available since there is no mixing at the point of dosage to optimise the chlorine exposure to microorganisms at the same time as chlorine reacts with competing substrates in the effluent. Chlorine reacts very rapidly at pH values of 6-9 and the process is essentially completed in a few seconds.

Based on the results of this study, in practice the current cost of disinfection by chlorine can be reduced by at least 50% since inactivation can be reached at less than 50% of the chlorine dose required to meet chlorine demand. In addition, this will create the possibility that the effluent discharged into the water course can have 0 mg/l free chlorine. Therefore, mixing chlorine at a point of dosage can constitute a new and good efficient method of disinfection.

5.2 Achievement of the Study's Objectives

This section concludes with reference to the objectives of this study to validate the original contribution of this report:

i. Since it is important to look at options to reduce chlorine demand and redirect chlorine dose to its primary aim of microorganism inactivation without the total chlorine demand being met, this study set out to empirically evaluate the impact of chlorine and wastewater contact time (Ct) and chlorine residual concentration on microorganism (specifically E. coli) inactivation. The literature survey presented in Chapter 2 and the results obtained in Chapter 4 show that, depending on the concentration of residual chlorine, available microorganisms that were not in contact (or exposed) to chlorine during dosing would be deactivated by the available chlorine residual during increased contact time. The required samples and test results for this investigation were generated at the Burgersfort wastewater treatment works. As can be seen in Chapter 4, gently and vigorous mixing of chlorine with wastewater achieved a reasonable degree of disinfection while using less chlorine. This consequently will save on chlorine dosing. This investigation can therefore assist relevant authorities at wastewater treatment plants to reduce the cost of chlorine used for disinfection.

ii. If the objective in the above bullet-point is achieved and free chlorine residual in the effluent is reduced to zero, this will address the problem faced by most wastewater treatment plants of discharging above zero free chlorine residual in the effluent into water bodies. This will be ecologically beneficial. Chapter 4 demonstrated the effect of mixing on E. coli inactivation. The results show that with gently and vigorous mixing at the at the chlorine dosage below breakpoint chlorination, free chlorine residual decrease to 0 mg/l as contact time increases.

iii. This study investigated the effectiveness of mixing at the point of chlorination. Chapter 4 demonstrated that rapid (vigorous) mixing of chlorine with wastewater achieved a higher degree of disinfection than partial (gently) mixing while employing the same chlorine dosage and contact time. In similar fashion, partial mixing achieved a higher degree of disinfection than no-mixing while employing the same chlorine dosage and contact time. It must be noted again that the chlorine dosage applied in these experiments are much less than that typically employed in most treatment works for microorganism inactivation. This, if applied in a treatment works, will result in cost savings on chlorine dosage to meet chlorine demand and produce expected chlorine residual. The study therefore reveals that the typical process control variables of contact time and chlorine concentration have a limited effect on the inactivation of particle-associated organisms but mixing effect at the dosing point, which also confirm the finding by Dietrich *et al.,* (2007).

iv. The above points shows that this study examined ways to reduce chlorine disinfection dosage for wastewater by reducing chlorine dose compared to the current chlorine dose practice, the cost of wastewater treatment will decrease due to (i) the decrease in the need to de-chlorinate high chlorine residual in the effluent before discharge and the decrease in chlorine dosage for microorganism inactivation. This is set out in Chapter 4.

5.3 RECOMMENDATIONS FOR FUTURE RESEARCH

As the water industry moves into the 21st century, design approaches will evolve in response to the need to provide more rigorous protection of public health from the risk of disinfection by-products. This balance of disinfection benefit and risk will continue to spur the industry to evolve towards more encompassing regulation, informed design and optimised operation. In particular, the use of disinfectants in excess of those needed to achieve the desired level of disinfection will result in an unnecessary increase in disinfection by-products and financial cost.

Given the limited scope of this study and the future context, it is imperative that future research studies look at the following research areas:

- The development of a detailed kinetic models representing chlorine's different reactions with inorganic and organic materials in solution, chlorine's interaction with microorganisms and chlorine's decomposition in the effluent based on the effect of mixing.

- The development of hydrodynamic model of the disinfection contactor, the chlorine dosage and mixing basin sizing for optimal retention times, as well as optimum velocity gradient within disinfection contact chambers.

- An integrated approach to disinfection design and operation that incorporates the characteristics of the chemical disinfectant, disinfection kinetic model by organism and the contactor hydraulic condition.

- The underlying physical, biological and/or chemical properties associated with the differences observed in parameter values that affect chlorine reaction and diffusion in wastewater effluent. The study may assist to identify upstream treatment processes that will remove particles that inhibit quick microorganism exposure in order to enhance disinfectant penetration into microorganisms.

In future waterworks should be designed to include mixing within the chlorine contact unit in order to provide maximum contact between the disinfectant and the microorganisms to be inactivated. The chlorine contact facility would then be considered an integral part of the overall wastewater treatment process, which means it would become a unit process such as sedimentation, aeration, and sludge digestion.

REFERENCES

Adewumi, J. R., Ilemobade, A. A and van Zyl, J. E 2010. 'Decision support for the planning of integrated wastewater reuse projects in South Africa'. *Water Science and Technology – Water Supply*, Vol. 10, no. 2, pp 251-267.

Adewumi, J. R., Ilemobade, A.A and van Zyl, J.E 2012, 'Minimizing risks in wastewater reuse: proposed operational principles and guidelines for South Africa', *Journal of Water Reuse and Desalination*, Vol. 2, no. 4, pp 227-238.

Acher, A.J., Fischer, E and Manor, Y 1993, 'Sunlight disinfection of domestic effluents for agricultural use'. *Water Res*. Vol. 28, pp. 1153-1160.

Amiri, F., Mesquita, M.M.F and Andrews, S.A 2010, 'Disinfection effectiveness of organic chloramines, investigating the effect of pH'. *Water Research*. Vol. 44, pp. 845-853.

Amiri, F., Mesquita, M.M.F and Andrews, S.A 2010, 'Disinfection effectiveness of organic chloramines, investigating the effect of pH', *Water Research*, Vol. 44, p. 845-853.

America Water Works Association 2002, *Disinfection of water storage facilities*, C652-2002, AWWA.

Charrois, J.W.A and Hrudey, S.E 2007, 'Breakpoint chlorination and free-chlorine contact time: Implication for drinking water N-nitrosodimethylamine concentration', *Water Research*, Vol 41, pp. 674-682.

Dai, J., Jiang, F., Shang, C, Chau, K., Tse, Y., Lee, C., Chen, G., Fang, J and Zhai, L 2013, 'The impact of chlorine disinfection on biochemical oxygen demand levels in chemically enhanced primary treatment effluent', *Water Science & Technology*, Vol 68, pp 380–386.

Debordea, M and von Guntena, U 2008, ‘Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review’, *Water Research*, Vol. 42, pp. 13–51.

DWAF, Department of Water Affairs and Forestry 1996, *South African water quality guidelines* (2nd edition), Vol. 2, Domestic Use. Pretoria, RSA (1996). Compilation of Water Quality Guidelines and Standard.

Dietricha, J.P., Logea, F.J., Ginna, T.R and *Basağaoğlub*, H 2007, ‘Inactivation of particle-associated microorganisms in wastewater disinfection: Modeling of ozone and chlorine reactive diffusive transport in polydispersed suspensions’ *Water Research*, Vol. 41, pp. 2189–2201.

Dietrich, J.P., Basagaoglu, H., Loge, F.J and Ginn, T.R. 2003, ‘Preliminary assessment of transport processes influencing the penetration of chlorine into wastewater particles and the subsequent inactivation of particle-associated organisms’, *Water Res*, Vol. 37, pp. 139–149.

Ducoste, J., Carlson, K., Bellamy, W 2001, The integrated disinfection design framework approach to reactor hydraulics characterization’, *J. Water Supply: Res. Technol.-Aqua*, Vol. 50 no. 4, pp. 245–261.

DWA, Department of Water Affairs 2009, *Municipal Wastewater Treatment: Base information for targeted risk-based regulation*: *(Limpopo Province),* 2009.

DWA, Department of Water Affairs 2011, *Green drop report 2011: Wastewater service regulation*, Republic of South Africa.

DWA, Department of Water Affairs 2012, *Green drop progress report 2012: Wastewater service regulation*, Republic of South Africa.

EPA Victoria, Environment Protection Authority Victoria 2002, *Guidelines for environmental managements: Disinfection of treated wastewater*. EPA Victoria, Publication 730. ISBN 0 7306 7623 4. Available from: www.epa.vic.gov.au/~/media/Publications/730.pdf, Accessed on 19 November 2012.

Lenntech, 2012, 'Factors that influence water disinfection'. Available from: http://www.lenntech.com/processes/disinfection/factors/factors-disinfection-water.htm, Accessed on September 2012.

Freese, S.D, Bailey, I and Nozaic, D 2003, *The evaluation of alternative disinfection processes for the removal of protozoan oocysts and cryts and other micro-organisms, in the treatment of final wastewater*, Water Research Commission Report no. 1030/1/03.

Gehr, R, Wagner, M, Veerasubramanian, P and Payment, P 2003. 'Disinfection efficiency of peracetic acid, UV and ozone after enhanced primary treatment of municipal wastewater', *Water Research*. Vol. 37, pp. 4573-4586.

Golder Associates Africa and Zitholele Consulting 2006a, 'Wastewater Treatment in South Africa: Field Evaluation of the Status and Performance of Wastewater Treatment Plants: Final'.Submitted to: Water Research Commission (WRC) and Department of Water Affairs and Forestry (DWAF).

Golder Associates Africa and Zitholele Consulting, August 2006b, Wastewater Treatment in South Africa: "From Crisis to Compliance" Final Report No: 8011/8295/3/P, Submitted to: Water Research Commission (WRC) and the Department of Water Affairs and Forestry (DWAF).

Government Gazette (No. 92250 1984 Regulation No. 991 18 May 1984: Requirements for the Purification of Waste Water or Effluent: General and Special Standards.

Government Gazette (No. 20526) 1999, *General and Special Authorisation - Discharge limits and conditions set out in the National Water Act*, (DWAF).

Headleya, T, Nivalaa, J, Kassaa, K, Olssonb, L, Wallacec, S, Brixb, H, van Afferdena, M and Müller, R 2013, 'Escherichia coli removal and internal dynamics in subsurface flow ecotechnologies: Effects of design and plants. Ecological Engineering', Available from: http://dx.doi.org/10.1016/j.ecoleng.2013.07.062, Accessed on 20 August 2013.

Helbling, D.M and VanBriesen, J.M 2007, Free chlorine demand and cell survival of microbial suspensions', *Water Research*, Vol. 41. pp. 4424–4434.

Ibanez, J.G, Hernandez-Esparza, M, Doria-Serrano, C, Fregoso-Infante, A, Singh, M.M 2008, 'Wastewater disinfection: Environmental Chemistry'. *Springer, New York.* pp 225-230.

Jeong, J., Kim, L.Y. and Yoon, J 2006, 'The role of reactive oxygen species in the electrochemical inactivation of microorganisms', *Environ. Sci. Technol*, Vol. 40 no. 19, pp. 6117–6122.

Kim, D, Stoesser, T, and Kim, J 2013, 'Modeling aspects of flow and solute transport simulations in water disinfection tanks. Applied Mathematical Modelling', Vol. 37, pp. 8039–8050.

Kim, H and Lee, S 2006, 'Pump diffusion flash mixing (PDFM) for improving coagulation process in drinking water treatment', *Separation and Purification Technology*, Vol. 52, pp 117–125.

Kim, H, Kwon, S, Han, S, Yu, M, Gong, S and Colosimo, M.F 2006, 'New process control strategy for wastewater chlorination and dechlorination using ORP/pH', *Water Science & Technology*, Vol. 53, No 4, pp 431–438.

Kitis, M 2004, 'Disinfection of wastewater with peracetic acid: a review', *Environment International*, Vol. 30, pp. 47–55.

Li, B and Zhang, T 2013, 'Different removal behaviours of multiple trace antibiotics in municipal wastewater chlorination', *Water Research*, Vol. 47. pp. 2970–2982.

Li, D, Zeng, S, Gu, A, He, M and Shi, H 2013, 'Inactivation, reactivation and regrowth of indigenous bacteria in reclaimed water after chlorine disinfection of a municipal wastewater plants', *Journal of Environmental Science*, Vol. 7, pp 1319-1325.

Li, D, Gu, A.Z, Zeng1, S, Yang, W, He, M and Shi1, H 2011, 'Evaluation of the infectivity, gene and antigenicity persistence of rotaviruses by free chlorine disinfection', *Journal of Environmental Sciences*, Vol. 23, no.10, pp 1691–1698.

Lim, M.Y, Ju-Mi Kim, J and Ko, G 2010, 'Disinfection kinetics of murine norovirus using chlorine and chlorine dioxide', *Water Research*, Vol. 4 4, pp 3243-3251.

Linvil, G.R 2002, *Nitrites and their impact on effluent chlorination*, Clemson University.

Longley, K.E 1978, 'Turbulence factors in chlorine disinfection of wastewater', *Water Research*, Vol. 12, pp. 813-822.

Macauley, J.J, Qiangb, Z, Adamsb, C.D, Surampallie, R and Mormilea, M.R, 2006, 'Disinfection of swine wastewater using chlorine, ultraviolet light and ozone', *Water Research*, Vol. 40. pp. 2017–2026.

MacCrehan, W.A, Bedner, M and Helz, G.R 2005, 'Making chlorine greener: Performance of alternative de-chlorination agents in wastewater', *Chemosphere*, Vol. 60, pp. 381–388.

Manus, L and Van der Merwe-Botha, M 2010, 'Raising wastewater treatment performance through incentive and risk-based targeted regulation,, *Proceedings of the 2010 Water Institute of South Africa (WISA)*, Durban, South Africa 18-22 April.

Marhaba, T.F, 2009, 'Monitoring Disinfectants', *Handbook of Water Purity and Quality,* Elsevier Inc, Chp. 12.

Metcalf and Eddy. 1991, *Wastewater engineering: treatment, disposal, and reuse,* McGraw-Hill, Sydney.

Momba, M.N.B and Makala, N 2004, 'Comparing the effect of various pipe materials on biofilm formation in chlorinated and combined chlorine-chloraminated water systems', *Water Research/Water SA,* Vol. 7, pp 175-182.

Momba, M.N.B, Osode A.N and Sibewu, M 2006, 'The impact of inadequate wastewater treatment on the receiving water bodies case study: Boffalo city and Nkokonbe municipalities of the Eastern Cape Province', *Proceedings of the 2006 Water Institute of South Africa (WISA),* Durban, South Africa.

NATIONAL WATER ACT, 1998. (Act No. 36).

Neumann, M.B, von Gunten, V and Gujer, 2007, 'Uncertainty in prediction of disinfection performance', *Water Research,* Vol 41, pp. 2371-2378.

Page, M.A, Shisler, J.L, and Marina, B.J 2009, 'Kinetics of adenovirus type 2 inactivation with free chlorine', *Water Research,* Vol. 43, pp. 2916-2926.

Pascho, R.J, Landolt, M.L and Ongerth, J.E 1995, 'Inactivation of Renibacterium salmoninarum by free chlorine', *Aquaculture,* Vol. 131, pp. 165-175.

Pretorius, P.C and Pretorius, W.A 1999, 'Disinfection of purified sewage effluent with monochloramine', *Water Research/Water SA,* Vol. 9, pp 463-471.

Rauen, W.B, Angeloudis, A and Falconer, R.A 2012, 'Appraisal of chlorine contact tank modelling practices', *Water Research*, Vol. 46. pp. 5834–5847.

Rudd, T and Hopkinson, L.M 1989, 'Comparisom of Disinfection Techniques for Sewage and Sewage Effluents', *J. IWEM*, Vol. 3, pp 612-618.

Shin, G and Sobseyb, M.D 2008, 'Inactivation of norovirus by chlorine disinfection of water', *Water Research*, Vol. 4, no.2, pp. 4562–4568.

Hendricks, L.B 2008, Minister of Water Affairs and Forestry: Statement/Speech to Parliament on 'water crisis', Parliament, Cape Town, Available from: http://www.dwa.gov.za/minister/Default_dates06.asp? year=2008, [11 March 2008].

Silva, G.H.R, Daniel, L.A, Bruning, H, Rulkens, W.H 2010, 'Anaerobic effluent disinfection using ozone: Byproducts formation', *Bioresource Technology*, Vol. 18, pp. 6981 – 6986.

Srinivasan, S Aslan, A, Xagoraraki, I, Alocilja, E and Rose J.B 2011, 'Escherichia coli, enterococci, and Bacteroides thetaiotaomicron qPCR signals through wastewater and septage treatment', *Water Research*, Vol. 45, No. 8, pp. 2561–2572.

Tyrrell, S.A, Rippey, S.R and Watkins, W.D 1995, 'Inactivation of bacterial and viral indicators in secondary sewage effluents, using chlorine and ozone', *Water. Research.* Vol. 29, No. 11, pp. 2483-2490.

Warriner, R, Kostenbader, K.D, Cliver, D.O, and Ku, W 1985, 'Disinfection of advanced wastewater treatment effluent by chlorine, chlorine dioxide and ozone', *Water Research*. Vol 19, pp. 1515-1526.

WATER SERVICES ACT, 1997. (Act No. 108).

White, G.C, 1999, ‘Disinfection of wastewater and water for reuse’, *Van Nastrand Reinhold Environmental Engineering Series*, pp. 104.

Wua, Q, Hua, H, Zhao, X and Li, Y 2010, ‘Effects of chlorination on the properties of dissolved organic matter and its genotoxicity in secondary sewage effluent under two different ammonium concentrations’, *Chemosphere*, Vol. 80. pp. 941–946.

Winwarda, G.P, Avery, L.M, Stephensona, T and Jeffersona, B 2008, ‘Chlorine disinfection of grey water for reuse: Effect of organics and particles’, *Water Research*, Vol. 42, pp.483–491.

Williams, M.L, Paimer, C.G and Gordon, A.K 2003, ‘Riverine macroinvertabrate responses to chlorine and chlorinated sewage effluent – Acute chlorine tolerance of Baetis harrisoni (Ephemeroptera) from two rivers in KwaZulu-Natal, South Africa’, *Water Research/Water SA*, Vol. 5, pp 483-488.