A Guide For The Design Of Chloramine Disinfection Facilities For Purified Sewage Effluent

by

WA Pretorius & PC Pretorius

**The University of Pretoria, Department of Chemical Engineering,
Water Utilisation Division**

Final Report To The Water Research Commission

WRC Report No: 739/1/01
ISBN No: 1 86845 811 3
November 2001

Executive Summary

A Guide For The Design Of Chloramine Disinfection Facilities For Purified Sewage Effluent

The aims of the project were as follows:

- To assess the current disinfection practices followed at South African sewage treatment facilities
- To conduct a review of the relevant literature
- To evaluate the performance of chloramine as an alternative to chlorine as a disinfectant under conditions typical of South African sewage treatment facilities
- To evaluate the accuracy of kinetic disinfection models found in the literature by doing batch and continuous flow inactivation studies in the laboratory.
- To prepare a practical guide for the design of disinfection facilities for purified sewage effluent.

The project documentation is contained in three parts:

The first part consists of the guide aimed at the design engineer of a sewage treatment facility. The guide contains an overview of the relevant literature and covering the basic chemical and biological aspects of disinfection. A section on the kinetics of the inactivation of microorganisms gives an overview of the development of mathematical models of disinfection. The disinfectant contact chamber and the factors affecting the process is discussed followed by step-by-step design example.

The second part reports the findings of a national survey conducted in 1996/1997 to which 175 sewage treatment plants responded. The survey showed that only a third of the total effluent flow complied to accepted bacteriological standards and that 67% of the total flow surveyed was discharged to public streams. These facts indicate the need for better design and operation of disinfection at sewage treatment plants in South Africa. This information is presented in Appendix A.

Part three is presented in Appendix B and reports the results of research conducted at the University of Pretoria. The aim of the research was to evaluate the efficiency of monochloramine as a disinfectant for purified sewage effluent under South African conditions. The research also identified the most suitable mathematical model for predicting the behavior of continuous flow disinfection using monochloramine. The use of tracer studies to predict the efficiency of a contact chamber is shown.

ACKNOWLEDGEMENTS

The authors wishes to thank the following:

All the respondents who contributed to the national disinfection survey,

the management and staff of the Zeekoegat and Brits waste water treatment facilities,

Mr. N.G.J. Oosthuizen

the members of the project steering committee

and the Water Research Commission

for their guidance, support and contributions towards the preparation of this dissertation.

TABLE OF CONTENTS

1 INTRODUCTION....1

2 CHLORINE....2

2.1 Chemical Properties and Occurrence....2

2.2 Physical Properties....2

2.3 Hydrolysis of Chlorine Gas....3

2.4 The Effect of pH and Temperature on Free Chlorine Speciation....4

3 THE CHEMISTRY OF WASTEWATER CHLORINATION....5

3.1 Nitrogenous Compounds of Interest to Wastewater Disinfection....5

3.2 The Breakpoint Curve....6

3.3 Organic Nitrogen....8

3.4 Other Organic Compounds....10

3.5 Inorganic Compounds....10

4 THE INDICATOR ORGANISM....11

5 THE KINETICS OF DISINFECTION....12

5.1 Factors Affecting the Rate of Inactivation of Micro-Organisms....12

6 THE DISINFECTION CONTACT CHAMBER....15

6.1 The Function of the Contact Chamber....15

6.2 Distribution of Residence Time....15

6.3 The Effect of Non-Ideal Flow on Disinfection....15

6.4 Effect of the Geometrical Design of the Disinfectant Contact Chamber....16

6.5 Baffles and Cleaning....16

7 DESIGN EXAMPLE 17

8 REFERENCES....20

APPENDIX A: FINDINGS OF THE NATIONAL DISINFECTION SURVEY

APPENDIX B: Water SA Article: Disinfection of purified sewage effluent with monochloramine.

LIST OF TABLES

Table 1: Properties of Liquid and Gaseous Chlorine 3

Table 2: Percent Molecular Chlorine and Hypochlorous Acid as a Function of pH and Solution Concentration 4

Table 3: Summary of the Conditions Required for the Formation of the Different Chloramine Species 6

Table 4: Some Examples of the Reactions of Chlorine Consuming Inorganic Species 11

Table 5: Summary of the Principle Inactivation Models 13

LIST OF TABLES

Figure 1: Distribution of HOCl and OCl^- at Different pH and Temperature Values 5

Figure 2: The Breakpoint Curve 3

Figure 3: The Effect of the Different TKN Fractions on the Disinfection of Nitrified Sewage Effluent 9

A Guide for the Design of Chloramine Disinfection Facilities for Purified Sewage Effluent.

1. Introduction

The South African General and Special Standards stipulate that purified sewage effluent, should comply to a standard of nil feacal coliforms/100ml (Act 96 of 18 May 1984 No9225, Regulation 991). This standard can only be achieved by disinfection. Various methods of disinfection are available including physical (e.g. ultra violet radiation) (Carnimeo, *et. al.,* 1994) and chemical processes (e.g. chlorine, chloramines, bromine and ozone) (Aieta, *et. al,* 1980; Jacangelo, *et. al.,* 1989).

The Division of Water Utilisation of the University of Pretoria was contracted by the Water Research Commission (WRC) to investigate the disinfection practices of sewage treatment plants in South Africa and to produce a guide for the design and operation of disinfection facilities. A National Disinfection Survey was conducted (1996/1997) and a total of 175 sewage treatment plants, treating a total flow of 2 million cubic meters per day, responded to a questionnaire set by the authors. According to White (1992) the most prevalent practice of wastewater disinfection in the United States is free chlorine ($HOCl + OCl^-$) this was also found to be the case in South Africa. It is also clear from the results of the survey (see Appendix A) that the disinfection of wastewater effluents in South Africa is not performed adequately. The fact that most of these effluents are discharged into public streams could pose a health risk.

There seems to exist some discrepancy between studies conducted to determine the disinfection efficiency of free chlorine and chloramines respectively. Studies conducted in the laboratory under chlorine demand free conditions and with cultured test bacteria have shown that free chlorine is a more effective disinfectant than the chloramines (Berman *et al.*, 1992; Kouame & Haas, 1991; Rice *et al.*, 1993; Ward *et al.*, 1984). These findings conflict with some field reports (that observe naturally occurring bacteria and water with a chlorine demand) that have shown that chloramines are adequate, and in some cases superior to free chlorine in terms of indicator organism reductions (Dice, 1985; Shull, 1981; Reynolds *et al.*, 1989; ASCE, 1986). Research conducted at the University of Pretoria (Pretorius & Pretorius, 1999) confirmed that monochloramine is an effective disinfectant for wastewater especially in the properly nitrified effluents common to South African wastewater treatment plant effluents. Case studies conducted on completely nitrified wastewater in the United States of America (see section 3.3) have shown that it is extremely difficult to properly disinfect these effluents with free chlorine and that ammonia should be present to form chloramines for successful disinfection. The use of chloramines for the disinfection of wastewater is therefore supported by both the literature and experiments conducted under typically South African conditions. This guide will be devoted to chloramine disinfection facilities for South African wastewater treatment plants.

It is important that both the designer and the operator of a disinfection system have at least some basic understanding of the properties of the disinfectant used, the major chemical processes involved, the kinetics of disinfection and the hydraulic

behaviour of the contact basin. It is the aim of this guide to provide the underlying theory and methods required to gain an understanding of chloramine based disinfection processes for purified sewage effluents.

2. Chlorine

To understand the disinfection of wastewater with chloramines it is necessary to know the physical and chemical properties of free chlorine and how these properties influence the formation of chloramine compounds. As free chlorine and the chloramine compounds differ significantly in their reactivity, it is important to have some insight in the reactions of free chlorine with impurities typically present in wastewater effluents. This underlines the fact that purified wastewater has a greater demand for free chlorine than for chloramines.

2.1. Chemical Properties and Occurrence.

The elements in Group 7 of the Periodic Table are known as the *halogens* ("salt-formers") (Masterton, *et al*., 1985). Chlorine (Cl) is a halogen that exists as a green to yellow diatomic gas (Cl_2) in the pure form. It is element number 17 on the periodic table and has an atomic mass of 35,457 g/mol. Because chlorine is highly reactive it is not found in its free form in nature, but rather in the anionic from of chloride (Cl^-, *halide* form) which makes up 0,15% of the earth's crust. Chloride is also the most abundant anion in sea water (c.a. 18,8 g/l) and serves as the natural resource for the production of most of the chlorine gas in the world today. The production of chlorine relies on the oxidation of the chloride ion to chlorine gas:

$$\mathbf{2Cl^-_{(aq)} \rightarrow Cl_{2\,(g)} + 2e^-} \qquad \mathbf{(1)}$$

The majority of industrial chlorine processes utilise this oxidation reaction using one of three types of electrolytic cells: diaphragm, mercury and membrane. All of these processes produce caustic soda concurrently with the chlorine.

2.2. Physical Properties

Elemental chlorine is a highly corrosive chemical and in the presence of moisture will destroy all ferrous metals including stainless steel. For this reason commercial chlorine gas is contained as a liquefied gas, in the absence of moisture, in steel containers. Chlorine has a characteristic pungent smell and is irritating to mucous membranes. Table 1 below is a summary of some of the physical properties of chlorine.

Table 1: Properties of Liquid and Gaseous Chlorine

Property	Units	Value
Specific gravity of gas	Relative to air = 1 at 0°C and 1 atm	2,482
Specific gravity of liquid	Relative to water = 1 at 0°C and 1 atm	1,41
Liquefying point	°C at 1 atm	-34,5
Freezing point	°C at 1 atm	-100,98
Solubility of gas in water	g/l	7,29
Compressibility of liquid	% / unit volume / atm increase	0,0018
Critical temperature	°C	144

Table 1 shows that chlorine gas has a specific gravity greater than air. This is of importance when considering safety as the gas will "sink" to the floor upon accidental release where workers may be exposed to the toxic fumes. The freezing point of chlorine may create some difficulty in the operation of chlorination equipment. If the rate of chlorine release from a cylinder is not carefully controlled the temperature of the dispensing equipment may fall rapidly resulting in the formation of crystals ("chlorine ice") that may block the flow of chlorine gas to the point of application. The high solubility of chlorine gas in water makes it easy to apply to water by injecting the gas into a relatively small side stream that is subsequently recombined with the main stream to be disinfected.

2.3. Hydrolysis of Chlorine gas

The most prevalent practice for handling chlorine is to dissolve the gas directly in water. The molecular chlorine undergoes a rapid hydrolysis to form hypochlorous acid (HOCl) as shown by the following reaction equation:

$$Cl_2 + H_20 \rightarrow HOCl + H^+ + Cl^- \qquad (2)$$

This equation shows how H^+ ions are released during the reaction. This is significant in that it lowers the pH and consumes alkalinity. It also shows that the relative abundance of Cl_2 and HOCl at equilibrium will be affected by pH. According to White (1992) the operation of chlorination equipment is always at partial pressures (vacuum) resulting in chlorine solubility values lower than the theoretical value. He recommends an upper limit of solubility of 3500mg/l. At this concentration the pH of the chlorinator discharge stream will have a pH no higher than 3 resulting in a significant frction of molecular chlorine at equilibrium (see Table 2). This situation leads to a number of practical considerations:

- Concentrations of higher than 3500 mg/l will cause excessive chlorine gas release at the point of application (degassing).
- Negative pressures in the chlorine solution piping will have an adverse effect on the hydraulic gradient.
- All systems that are not closed should be designed to avoid negative pressures conditions in the chlorinator solution lines.

The relationship between the molecular chlorine to hypochlorous acid ratio, pH and chlorine solution concentration is shown in Table 2 (from White 1992).

Table 2: Percent molecular chlorine (Cl_2) and hypochlorous acid (HOCl) as a function of pH and solution concentration.

pH	Solution Concentration (mg/ℓ Cl_2)									
	500		1000		1500		2000		3500	
	Cl_2	HOCl	Cl_2	HOCl	Cl_2	HOCl	Cl_2	HOCl	Cl_2	HOCl
1	54,30	45,65	64,67	35.25	69.94	29.95	73.29	26.57	78.91	20.89
2	17,66	82,31	27,41	72.52	33.95	65.93	38.78	61.05	49.70	49.97
3	2,48	97,51	4.73	95.25	6.79	93.17	8.68	91.26	13.57	86.28
4	0,26	99,72	0.52	99.46	0.77	99.20	1.02	98.45	1.76	98.18
5	0,026	99,74	0.05	99.71	0.078	99.68	0.104	99.66	0.181	99.58
6	0,000	97,68	0.005	97.67	0.008	97.67	0.010	99.67	0.018	97.66

The table shows that at high Cl_2 concentrations and low pH, a significant percentage of the chlorine is present in the dissolved molecular form. This could cause problems in that off gassing of chlorine may occur at the point of dosing if it is attempted to apply excessively high amounts of chlorine to the dosing stream. This is both wasteful and a safety risk.

2.4. The Effect of pH and Temperature on Free Chlorine Speciation

The hypochlorous acid formed by the hydrolysis reaction of Cl_2 and water is a weak acid and will therefore dissociate partially (pKa = 7,54):

$$HOCl \rightarrow H^+ + OCl^- \qquad (3)$$

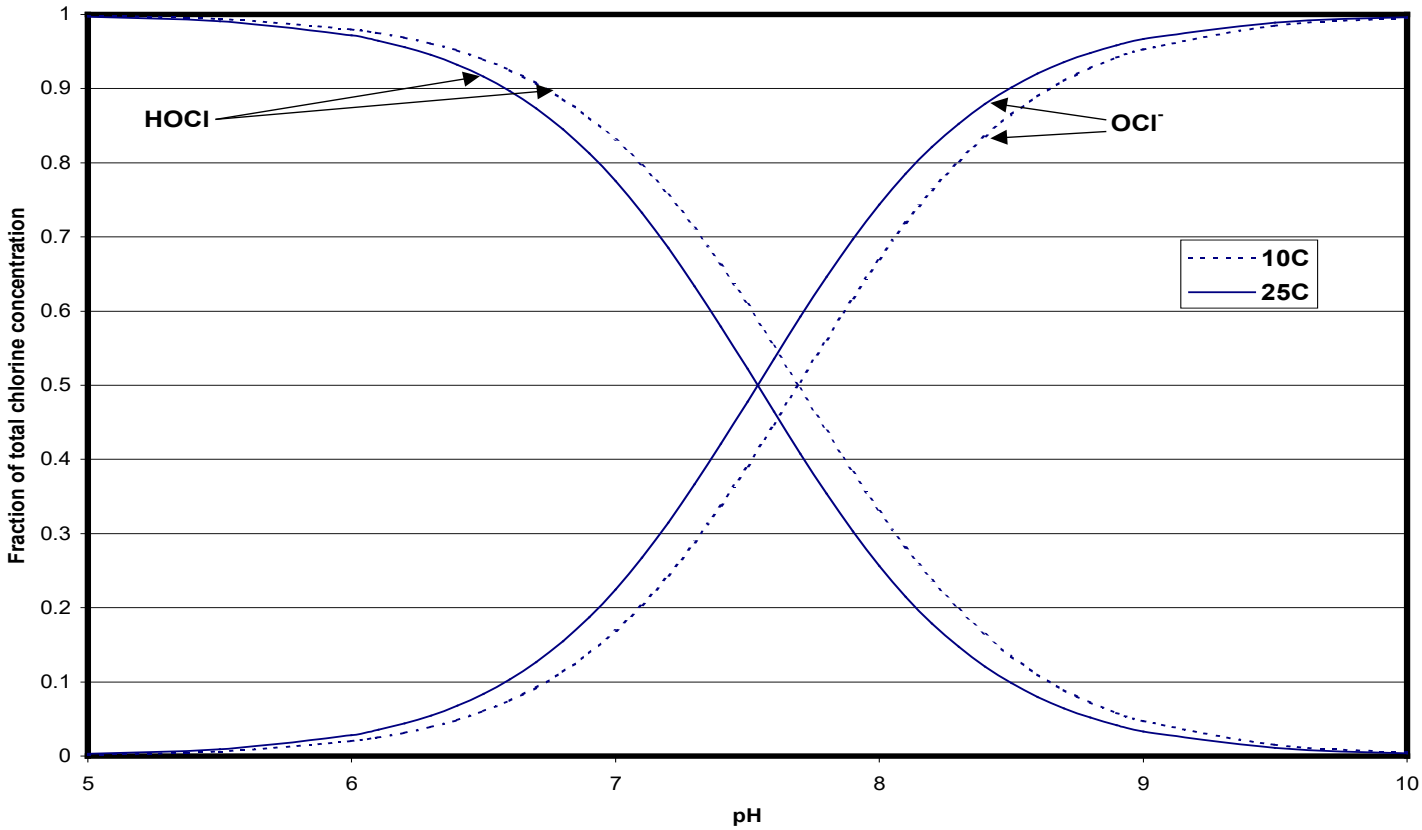


Figure 1: Distribution of HOCl and OCl^- at different pH and temperature values.

This is an important reaction in the disinfection of wastewater with chlorine as HOCl and OCl^- have different disinfective capabilities. The sum of HOCl and OCl^- concentrations is called the *free chlorine* concentration. The relative abundance of HOCl and OCl^- is affected by both pH and temperature as shown in **Figure 1**. The figure shows that pH has a much more pronounced effect upon free chlorine speciation than temperature does. At pH values above 7,5 to 7,6 OCl^- is the dominant species and disinfection becomes increasingly less effective at higher pH values as OCl^- is a much less effective disinfectant than HOCl.

3. The Chemistry of Wastewater Chlorination

3.1. Nitrogenous compounds of interest to wastewater Disinfection

The nitrogen compounds present in wastewater effluent can be divided into two groups i.e. inorganic nitrogen and organic nitrogen. Inorganic nitrogen compounds of interest to wastewater disinfection includes ammonia (NH_3) and nitrite (NO_2^-). Organic nitrogen compounds are mainly of proteinaceous origin. These compounds are usually proteins and amino acids. In the reaction of chlorine with nitrogenous compounds of the form NH_nR_{3-n} (e.g. NH_3 and amino acids) and chlorine, a N-Cl bond forms. The resulting group of compounds are called N-chloro compounds or chloramines. Chlorine in this

form is known as *combined chlorine*. The chloramines are further classified as inorganic (formed from NH_3) and organic (formed from organic nitrogen compounds such as amino acids).

3.2 The breakpoint curve

Three different inorganic chloramine compounds are formed during the chlorination of wastewater containing NH_3. These compounds form by successive substitution of the hydrogen atoms of the ammonia molecule with chlorine atoms as shown by the following reaction equations:

$$\mathbf{NH_3 + HOCl \rightarrow NH_2Cl\ (monochloramine) + H_2O} \quad \mathbf{(4)}$$

$$\mathbf{NH_2Cl + HOCl \rightarrow NHCl_2\ (dichloramine) + H_2O} \quad \mathbf{(5)}$$

$$\mathbf{NHCl_2 + HOCl \rightarrow NCl_3\ (trichloramine) + H_2O} \quad \mathbf{(6)}$$

The rates of these competing reactions as well as the relative amounts of each of the inorganic chloramines formed are dependent upon the following factors:

- temperature
- pH
- the chlorine to ammonia nitrogen mass ratio (Cl_2:NH_3-N)
- initial free chlorine and ammonia concentrations

The effect of temperature is to increase the reaction rate with increasing temperature.

Table 3 illustrates the effect of pH and the Cl_2:NH_3-N mass ratio on the rates of formation of the different chloramine species. The table shows how a higher degree of hydrogen substitution is favoured by low pH values, high Cl_2:NH_3-N mass ratios and slower reaction times. By controlling these parameters it is possible to selectively produce for example monochloramine. This is applied in practice in the chlorine-ammonia disinfection process also known as chloramination.

Table 3: Summary of the conditions required for the formation of the different chloramine species

Parameter	Monochloramine	Dichloramine	Trichloramine
Optimal pH for formation	8,3	5 - 7	<5
Cl_2:NH_3-N mass ratio	$\leq$ 5:1	5:1 to 10:1	10:1 to 15:1
Reaction time	0,2 to 0,07 seconds for 99% conversion	1hour for 90% conversion at pH 7	ND

ND = No Data given as little is known about the kinetics of this reaction.

The reactions in Eq 4 to 6 is of great importance in the practice wastewater chlorination.

As the chlorine dose is increased in the pH range of 6 to 8, found in most purified sewage effluents, the formation of monochloramine proceed as shown in Eq 4 up to a Cl_2:NH_3-N mass ratio of 5:1 (which is equivalent to a 1mol of Cl_2 :1mol of NH_3-N). The concentration of total chlorine residuals does not however continue to increase with further addition of chlorine but actually decreases up to a Cl_2:NH_3-N mass ratio of 7,6:1. At this point the total chlorine residual (free chlorine + combined chlorine) reaches a local minimum concentration and further additions of chlorine produce free chlorine residuals. The point where free chlorine appears is called the *breakpoint*. The variation of total chlorine residual with increasing chlorine dose described above may be presented on the *breakpoint curve* (See Figure 2). This behaviour is explained by the following equation presenting the overall *breakpoint reaction*:

$$\mathbf{2NH_3 + 3Cl_2 \rightarrow N_2 + 6H^+ + 6Cl^-} \qquad \mathbf{(7)}$$

This reaction explains the disappearance of combined chlorine residials between the peak and trough on the curve where combined chlorine in the form of mono- and dichloramine is completely oxidized to gaseous nitrogen. Only when all the ammonia nitrogen is destroyed in this manner is it possible for free chlorine to dominate.

Although this oxidation reaction competes with the trichloramine formation reaction, it dominates in the pH range of 6 to 8. At higher pH values the oxidation of ammonia is incomplete resulting in the formation of nitrate, while at lower pH values increasing amounts of trichloramine is formed.

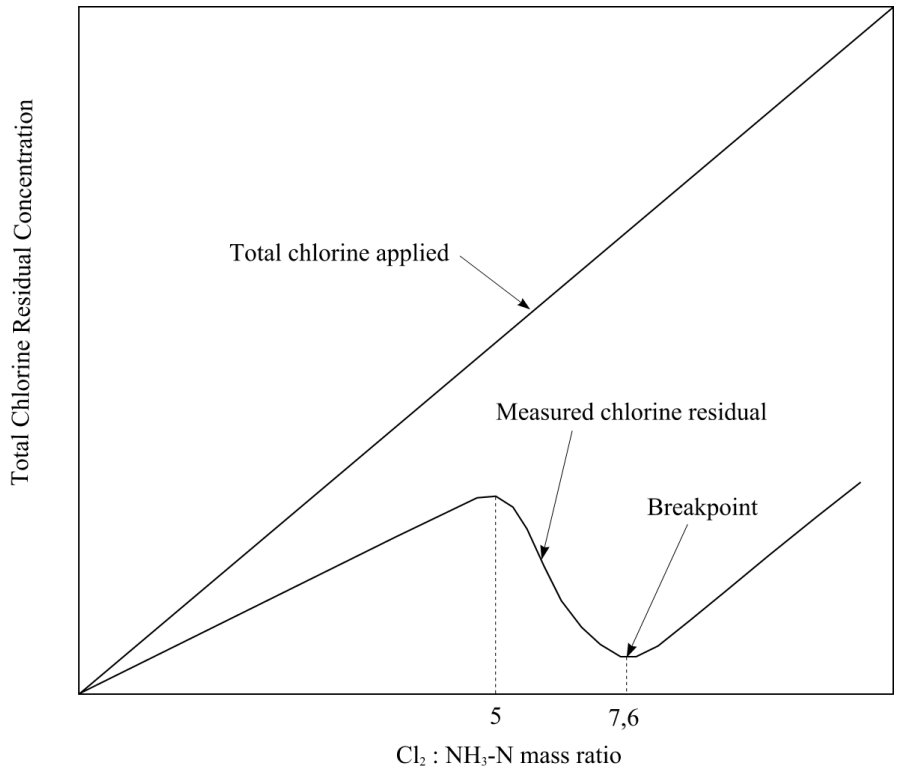


Figure 2: The breakpoint curve

The significance of the breakpoint phenomenon to the disinfection of wastewater is as follows:

- If wastewater in the pH range of 6 to 8 contains NH_3 it will consume Cl_2 at 7,6 mg of Cl_2/mg of NH_3-N present. This leads to a wasteful addition if more chlorine is added than is required for disinfection alone.
- The disinfective power of chlorine is dependant upon its chemical form with free chlorine being more powerful than the combined forms of chlorine.
- If a disinfection process relies upon free chlorine to inactivate organisms, the chlorine will have to exceed the breakpoint in order to ensure the presence of a free chlorine residual.
- The shape of the breakpoint curve is dependant upon pH, ammonia concentration, temperature and contact time and will therefore vary from one wastewater to another.

3.3. Organic Nitrogen

All wastewater of domestic origin contain organic nitrogen compounds. These compounds are mainly derived from proteinaceous substances and the organic nitrogen compounds of urine. The interaction between organic nitrogen compounds and chlorine is different to that of ammonia and chlorine. Chlorine reacts with organic nitrogen to form N-chloro compounds or organic chloramines that are relatively stable compounds and are therefore not completely oxidised during the contact times and with chlorine dosages normally found in wastewater disinfection. The practical importance of organic nitrogen compounds is as follows:

- The organic chloramines have virtually no disinfective capability and will consume chlorine without contributing to disinfection.
- The organic chloramines interfere in the chemical analysis of chlorine residuals by appearing as dichloramine.
- The net effect is a reduction in the germicidal efficiency of the total chlorine residual and an increase in the overall chlorine demand.

According to Ekama *et al.,* the Total Kjeldahl Nitrogen (TKN) of the influent to South African municipal wastewater treatment plants can be divided into the following fractions (Ekama *et al.* 1984):

- Free and saline ammonia (~75%)
- Biodegradable organic nitrogen (~12%)
- Unbiodegradable particulate nitrogen (~10%)
- Unbiodegradable soluble nitrogen (~3%)

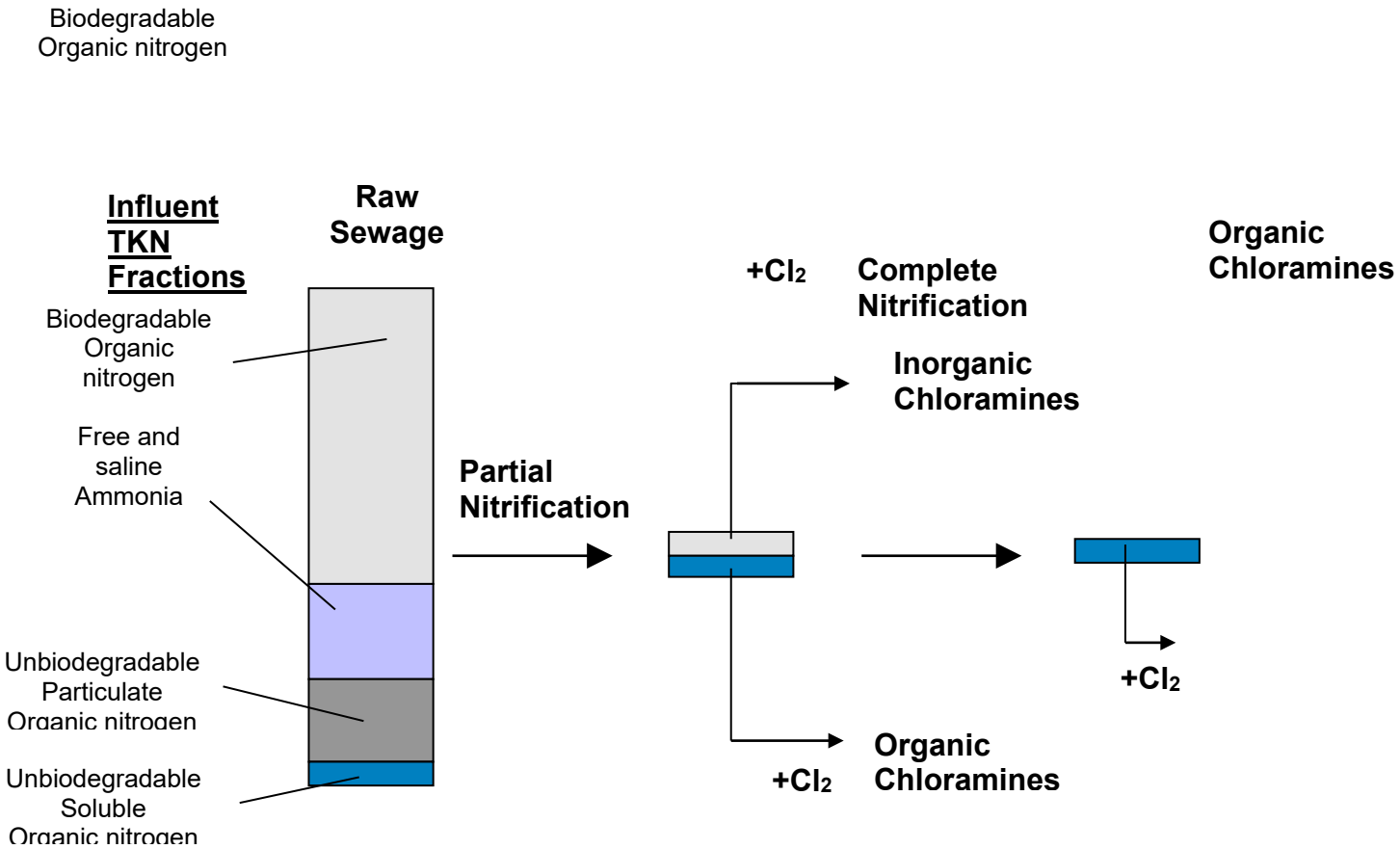


Figure 3: The effect of the different TKN fractions on the disinfection of nitrified sewage effluent.

Figure 3 shows how the different fractions of the influent TKN changes during treatment of the wastewater. After partial nitrification only two fractions remain, i.e. ammonia and unbiodegradable soluble nitrogen fraction. If the effluent of a treatment plant that only partially nitrifies is chlorinated, two possible products are formed, namely, inorganic chloramines and organic chloramines. If the process employs complete nitrification only the unbiodegradable soluble nitrogen fraction remains resulting in the formation of only organic chloramines upon chlorination. As the majority of South African treatment plants employ the activated sludge process it can be expected that the effluent will contain virtually no ammonia (complete nitrification) and that organic chloramines will be the dominant chlorinated product.

The effect that this phenomena has on the disinfection of wastewater is well documented by White *et al.,* who conducted an investigation on a number of US treatment plants that experienced difficulty in disinfecting nitrified effluents (White *et al.,* 1983). The investigation revealed that the plants that had nitrified effluents

required chlorine dosages more than twice as high (up to 22mg/l) as the plants that did not nitrify the effluent. This was because the free chlorine added to the water first reacted with organic nitrogen compounds (to form organic chloramines) as well

as other impurities present in the effluent before the demand could be satisfied and free chlorine could be present. The study also found that when chlorine was added to a completely nitrified effluent there will usually be an organic chloramine concentration of about 3mg/l. As the organic chloramines have no disinfection capability it was recommended that the ammonia in the effluent be controlled at a level of 2-3mg/l (partial nitrification) or that ammonia be added to the effluent after complete nitrification as it is very difficult

to control the ammonia concentration in the effluent to any reliable degree. One plant realised a 4,1% saving on its total operating budget by following this advice (Bhupinder, 1981).

The significance of the research reported above to disinfection of purified sewage effluents can be summarised as follows:

- The majority of treatment plants in South Africa have very low ammonia levels in the effluent resulting in limited disinfection efficiency.
- **Disinfection systems should be designed and operated using inorganic chloramines as the disinfectant by allowing for the addition of ammonia to completely nitrified effluents.**

3.4. Other organic compounds

The reaction between chlorine and organic compounds have become the source of some debate since the early seventies when it was discovered that certain disinfection by-products (DBP's) was formed during the chlorination of drinking water. A benefit of using chloramines is a reduction in the formation of THM's as reported by Reynolds, *et al.,* (1989). The best known example is a group of halogenated organic compounds called trihalomethanes (THM's) that have been proven to be toxic and possibly carcinogenic. There seem to be disagreement in the scientific community as to the extent of the health risk associated with THM's and other DBP's and that this risk should be balanced against the risk of inadequate disinfection. Apart from the formation of DBP's, chlorine will oxidise organic compounds to higher oxidation states with a reduction of chlorine to chloride. This consumption of chlorine will add to the overall chlorine demand of the water.

3.5. Inorganic compounds

The ability of free chlorine to act as a strong oxidising agent is the most useful of its properties. It is this oxidative power that enables it to disinfect and act as a bleaching agent. Unfortunately free chlorine does not selectively react with the organisms to be inactivated but will also rapidly react with any oxidizable chemical it encounters in the water environment. This has important implications for wastewater chlorination as sewage effluent consists of a complex mixture of chemicals that will rapidly react with chlorine. Research conducted in the USA have shown that up to 10% of the chlorine consumed at a wastewater treatment plant was consumed by nitrite and compounds other than ammonia and organic

compounds (White, G.C. and Beebe , R.D. 1983). The chlorine demand created in this way consumes chlorine before it has sufficient contact time to disinfect the water.

In the reaction of free chlorine with the chlorine demand of the water, it is destroyed and converted to the chloride ion. The addition of free chlorine to water and its subsequent destruction can be represented by the following equations (Griffin, AE and Chamberlin, NS (1941):

$$\mathbf{Cl_2 + H_2O \rightarrow HOCl + HCl} \quad \mathbf{(8)}$$

$$\mathbf{HOCl + (Chlorine\ demand) \rightarrow HCl + (oxidized\ compounds)} \quad \mathbf{(9)}$$

$$\mathbf{Overall: Cl_2 + H_2O + (Chlorine\ demand) \rightarrow 2HCl + (oxidized\ compounds)} \quad \mathbf{(10)}$$

The hydrochloric acid produced by this reaction will further react with the alkalinity of the water:

$$\mathbf{2HCl + H_2O + CaCO_3 \rightarrow CaCl_2 + CO_2 + 2H_2O} \quad \mathbf{(11)}$$

This reaction shows that chlorination of water can cause a drop in pH if sufficient alkalinity is not available to buffer the reaction. Table 4 presents a summary of some chemical species that will consume chlorine in a redox reaction. Because of the complex nature of wastewater it is not possible to know the exact type and amount of all the compounds that will be oxidised by chlorine. It is possible, however to measure the chlorine demand of a wastewater sample as an aggregate property.

Table 4: Some examples of the reactions of chlorine consuming inorganic species.

Species	**Reaction**	**Cl_2 demand (mg Cl_2)**
NO_2^-	$HOCl + NO_2^- \rightarrow NO_3^- + HCl$	5,06/mgNO_2^--N
Fe^{2+}	$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$	0,64/mgFe^{2+}
Mn^{2+}	$Mn^{2+} + Cl_2 + 2H_2O \rightarrow MnO_2 + 4H^+ + 2Cl^-$	1,29/mgMn^{2+}
H_2S	$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$	8,34/mgH_2S
CN^-	$5Cl_2 + 10OH^- + 2CN^- \rightarrow 2HCO_3^- + 10Cl^- + N_2 + 4H_2O$	6,82/mgCN^-
C	$C + 2Cl_2 + 2H_2O \rightarrow 4HCl + CO_2$	11,82/mgC
Alkalinity	Cl_2 + (Chlorine demand) + $CaCO_3 \rightarrow CaCl_2 + CO_2$ + (oxidised compounds)[1]	1,4mg Alkalinity as $CaCO_3$/mgCl_2 consumed

[1] Stoichiometry dependant on oxidation state of demand-causing materials

4.The Indicator Organism

The microbiological composition of wastewater and purified wastewater is extremely diverse. Some of the micro-organisms found in this complex mixture has the potential to cause disease and are called pathogenic organisms. The aim of disinfection of purified wastewater is to either reduce or eliminate these pathogenic organisms completely, depending upon the effluent quality required. It is therefore necessary to measure the microbiological quality of purified sewage effluent before and after the disinfection process to ensure it operates effectively. It would be impossible to characterise such waters by isolating and counting individual pathogenic species. It is for this reason that testing methods, that do not rely on the isolation of pathogens, have been developed.

These methods measure the presence of micro-organisms that indicate the possibility that pathogenic organisms may also be present and are therefore called *indicator* organisms. In the case of wastewater disinfection, the indicator organism is used as evidence of water pollution by faecal matter originating from humans or other warm blooded animals. The following are some properties that an indicator organism should ideally have:

- It should be present in water polluted with pathogens (in greater numbers) and absent when pathogens are absent.
- There should be a correlation between the numbers of the indicator organisms and the pathogens.
- It should be able to survive better and longer than the pathogens.
- It must have stable properties and be easily detected by standard laboratory tests.

Escherischia coli, a member of the coliform group of bacteria, is the organism that most closely satisfies these requirements. *E. coli* is a normal inhabitant of the intestines of warm blooded animals and humans. The General and Special standards specifies only the Faecal coliform group as the indicator organism for wastewater treatment plant effluents. Standard testing methods are available for the detection of pathogenic viruses, bacteria, fungi and protozoa (APHA, 1995).

5. The Kinetics of Disinfection

5.1. Factors affecting the rate of inactivation of micro-organisms

- **Contact time**

This is one of the most important factors affecting the disinfection process. It has been observed that the greater the contact time (for a given concentration of disinfectant) the greater the degree of inactivation of the target organisms. This observation was first formulated in the literature by Chick and was modified by Watson in the same year to take the effect of disinfectant concentration into account. This yielded the Chick-Watson law (see Eq 12, Table 5).

It is common to find that inactivation rates do not follow the Chick-Watson rate law. Rates of kill have been found to increase with time in some cases and to decrease with time in other cases. To account for these deviations from the Chick-Watson law Hom (1972) developed the relationship represented by Eq 13 and 14 in Table 5.

Equation 15 is known as the series-event kinetic model and was proposed by Severin *et al.,* in 1984. This equation models the disinfection process as a series of reactions between the target organism and the disinfectant until some lethal threshold number is reached (the integer j in Eq 15) and the organism is inactivated.

As discussed before (Section 3) free chlorine is a reactive chemical that will decay when it comes into contact with wastewater. This decrease in disinfectant concentration over time affects the rate of inactivation and is taken into account by Eq 16, presented by Haas *et al.* (1998).

Table 5: Summary of the principle inactivation models.

Model	Eqn.	Author	Comments
$\ln\frac{N_t}{N_o} = -kC^n t$	(12)	Chick/Watson (1908)	First order with respect to surviving bacteria if C is constant. k is the pseudo first order reaction rate constant and n is the coefficient of dilution.
$\ln\frac{N_t}{N_o} = -kC^n t^m$	(13)	Hom (1972)	Model developed to account for deviations from the Chick-Watson model in practice. m is an empirical constant and k and n are as for Eqn (1).
$\ln\frac{N_t}{N_o} = -k't^m$	(14)	Hom (1972)	Modification of Eqn(2) for constant disinfectant concentration. $k' = kC^m$ in Eqn (2).
$\frac{N_t}{N_o} = e^{-kct}\sum_{i=0}^{j-1}\frac{(kct)^i}{i!}$	(15)	Severin (1984)	The series event kinetic model where k is the mixed second-order reaction rate constant and j is an integer representing the lethal number of reactions for a single organism. The term kC may be replaced by K, the apparent kinetic constant
$\ln\frac{N_t}{N_o} = -\left(\frac{m}{nk^*}\right)^m k(C_o)^n\left[1-\exp\left(-\frac{nk^*t}{m}\right)\right.$	(16)	Haas, *et al* (1998)	A modification of the Hom model developed to take residual disinfectant decay into account. k, m and n are the same as for Eqn (2). C_o is the initial disinfectant concentration and k* the first order residual decay rate.

N_o = initial concentration of organisms k = reaction rate constant k^* = first order residual decay rate
N_t = organism concentration at time t m = empirical constant j = lethal number of reactions
C = disinfectant concentration n = coefficient of dilution

The equations given in Table 5 assumes identical contact times for all of the target organisms in a sample, i.e. a batch process. This is not the case for a disinfection contact chamber where the contact time is not identical for all organisms passing through the chamber, but is a function of the hydraulic behaviour of the chamber. The models in Table 5 must therefore be modified to take the hydraulic behaviour of the chamber into account if they are to be used to predict the behaviour of the disinfection process.

- **Concentration and Type of Disinfectant**

The type of disinfectant used will be the factor that has the greatest influence on a disinfection process. This is because different chemical agents have different disinfectant capabilities. These disinfectant powers have previously been measured under demand free conditions which removes the effect of water quality and makes it difficult to predict the relative strengths of disinfectants in a complex solution such as purified wastewater. If the strength of different disinfectants are therefore compared, inactivation studies should be conducted on the water to be disinfected so that a realistic and practical answer is obtained. The effect of the concentration of a specific disinfectant is to increase the rate of inactivation with increasing disinfectant concentration.

- **Number and type of target organisms**

The greater the number of organisms the greater the time required to achieve a specific percentage kill. However, this factor does not greatly influence the rate of inactivation of target organisms in a wastewater disinfection system. This is because:

- the concentration of organisms does not vary over a wide range over time and
- in a dilute system such as wastewater, the concentration of organisms is not a major consideration.

The effectiveness of the disinfectants will be influenced by the type and physiological condition of the micro-organisms. For example, viable growing bacteria cells are killed easily. In contrast, bacterial spores and protozoan cysts are extremely resistant, and many disinfectants have little effect on them.

- **Water Quality**

The chemical quality of the effluent to be disinfected will affect the demand that the effluent has for the disinfectant used. This was extensively shown for completely nitrified effluents (Section 3) that have a large demand for free chlorine but little or no demand for the chloramine compounds. This will result in a rapid decay of free chlorine while the chloramine concentration will remain relatively stable throughout the contact period. The quality of the effluent may therefore result in better disinfection results for one disinfectant that may show poor capabilities compared to another when tested in demand free water in the laboratory.

6. The Disinfection Contact Chamber

6.1 The Function of the contact chamber

The disinfectant contact chamber provides the physical structure where the wastewater and the disinfectant are brought into contact and must be designed so that optimal contact time is allowed between the disinfectant and the target organisms to be inactivated. As it is not the function of the contact chamber to mix the disinfectant and the effluent arrangements should be made for proper mixing before the effluent enters the contact chamber.

6.2 Distribution of Residence Time

Not all the elements of a fluid pass through a reactor along the same flow path and some short circuiting may take place. This creates a distribution in the residence time as shown by Levenspiel (1972: 255) of the different fluid elements, called the residence time distribution (RTD) . Tracers are used to measure the RTD of a reactor. The tracer is injected at the influent to the reactor and measured as it exits . The resulting response curve may then by analysed by means of mathematical models. Three models are available for this analysis: the tanks-in-series model, the dispersion index model and indices calculated from single points on the response curve. The design examples given in this guide employs only the tanks-in-series model.

The tanks-in-series model assumes that the flow through a real reactor may be represented as though it flows through a series of equally sized completely stirred tank reactors (CSTR's) (Levenspiel, 1972: 290). The number of CSTR's, N, is obtained by comparing the tracer response curve of a reactor to the theoretical response of a known number of CSTR's. Values of N range between two theoretical extremes (Smith, 1981: 283), i.e. N = 1 (a completely mixed reactor) and N = ∞ (a plugflow reactor). One of the advantages of the tanks-in-series model is that it uses all measured data and not only single points on the response curve.

The tanks-in-series model is used to evaluate tracer data obtained in this study because mathematical models already exist that combine batch disinfection data with a tanks-in-series model as shown by Severin, *et al* (1984). It was also shown to accurately predict the behaviour of laboratory scale continuous flow disinfection chambers (Pretorius & Pretorius, 1999).

The RTD of two chambers with identical volume and flow rate may differ significantly if geometrical configuration of the chambers are different. The ideal disinfection contact chamber is one in which no short circuiting takes place i.e. a perfect plug flow reactor.

6.3 The Effect of non-ideal flow on disinfection

A batch reactor (beaker) shows behavior identical to a perfect plug flow reactor. In a full scale disinfection contact chamber this is not the case and some residence

time distribution will exist. This residence time distribution (i.e. short circuiting) can have a negative impact upon the efficiency of the disinfection system. This is because the organisms contained within in the short circuiting fluid will be exposed to the disinfectant for a shorter period of time than the rest of the fluid. This portion of the fluid will therefore require a correspondingly higher disinfectant concentration to achieve an effective inactivation of organisms. This higher disinfectant dose must be applied to the total flow resulting in higher disinfectant usage than would be required for a plug flow chamber. This principle shows that the design criterion of theoretical residence time (chamber volume divided by flow rate (V/Q)) is not adequate for the design of disinfectant contact chambers as it does not take the hydraulic behavior of the chamber into account. For example, there may be difference of orders of magnitude in the bacterial kill in the two reactors with identical contact times but different geometrical designs. The geometrical design of a disinfectant contact chamber is therefore of primary importance to its efficiency.

6.4 Effect of the geometrical design of the disinfectant contact chamber.

- **The length to width ratio**

A field study by Marske and Boyle (1973) (as reported by White, 1992) evaluated seven different chamber configurations. The study indicated that the plug flow characteristics usually increased with increasing *L/W* ratio, but the correlation is poor. The ones with longitudinal baffles proved to be the most efficient. The one with the most ideal flow regime was found to be a longitudinally baffled chamber with a flow length to width ratio of 72:1 and provides 95 percent plug-flow conditions. By eliminating of the square corners in the tank it is possible to improve the efficiency of the chamber even further. This work substantiates the claims that long, narrow channels and/or conduits make the best chlorine contact chambers.

- **Depth to Width Ratio *(H/W)***

A contact chamber analysis by Trussell and Chao (1977) shows that depth can have an effect on the RTD of the chamber but not nearly to the same extent as the length to width ratio. Based-upon the results of a plant-scale Sepp and Bao (1980) the data indicate the *H/W* ratio should be 1.0 or less. Therefore a compromise is a square cross-section at peak flow (maximum water surface) and a slightly rectangular section at lower flows (White, 1992).

6.5 Baffles and cleaning

Longitudinal baffles provide better disinfection efficiency than horizontal baffles. The latter creates much more short-circuiting and back-mixing in the chamber than longitudinal baffles. The concrete in the contact basins should smooth finish to avoid creating areas where bacteria may escape disinfection and multiply. Contact basins should be cleaned frequently and must be kept as free from slime and algae deposits as a well-kept swimming pool. It is known that 50 percent of the suspended solids remaining in the effluent will settle in the contact chamber.

Therefore the contact chamber must be provided with a means for easy cleaning on a regular basis.

7. Design Example

The following example is included to show how the method discussed above can be applied to a situation where a chloramination system is to be retrofitted to an existing CCT. The following data is available
Table A1: Available data

Parameter	Units	Value
Volume of CCT (V)	m^3	450
Flow rate (F)	m^3/min	30
Theoretical Hydraulic retention time (T)	min	15
Design Ph	pH	7,0
Desired effluent feacal coliform count	CFU/100 ml	<1
Initial feacal coliform count	CFU/100 ml	100 000

The objective is to determine the monochloramine concentration required to obtained a desired inactivation of feacal coliform bacteria.

Step 1:
Conduct a tracer study on the CCT's and analyse the data with the tanks-in-series model. The following table contains typical data obtained from a tracer experiment where 400g of Lithium was injected as a pulse input into the CCT described in table A1:

Table A2: Data obtained from tracer study.

Time (min)	Lithium concentration (mg/l)	θ	Cθ	Recovery of lithium (g)
1	0,03	0,07	0,03	0,80
2	0,02	0,13	0,03	0,69
3	0,04	0,20	0,04	1,07
4	0,03	0,27	0,03	0,91
5	0,04	0,33	0,04	1,07
6	0,04	0,40	0,05	1,25
7	0,14	0,47	0,15	4,11
8	0,36	0,53	0,40	10,75
9	0,50	0,60	0,56	14,88
10	0,77	0,67	0,87	23,10
11	0,95	0,73	1,06	28,37
12	1,16	0,80	1,30	34,65
13	1,23	0,87	1,39	36,96
14	1,25	0,93	1,41	37,60

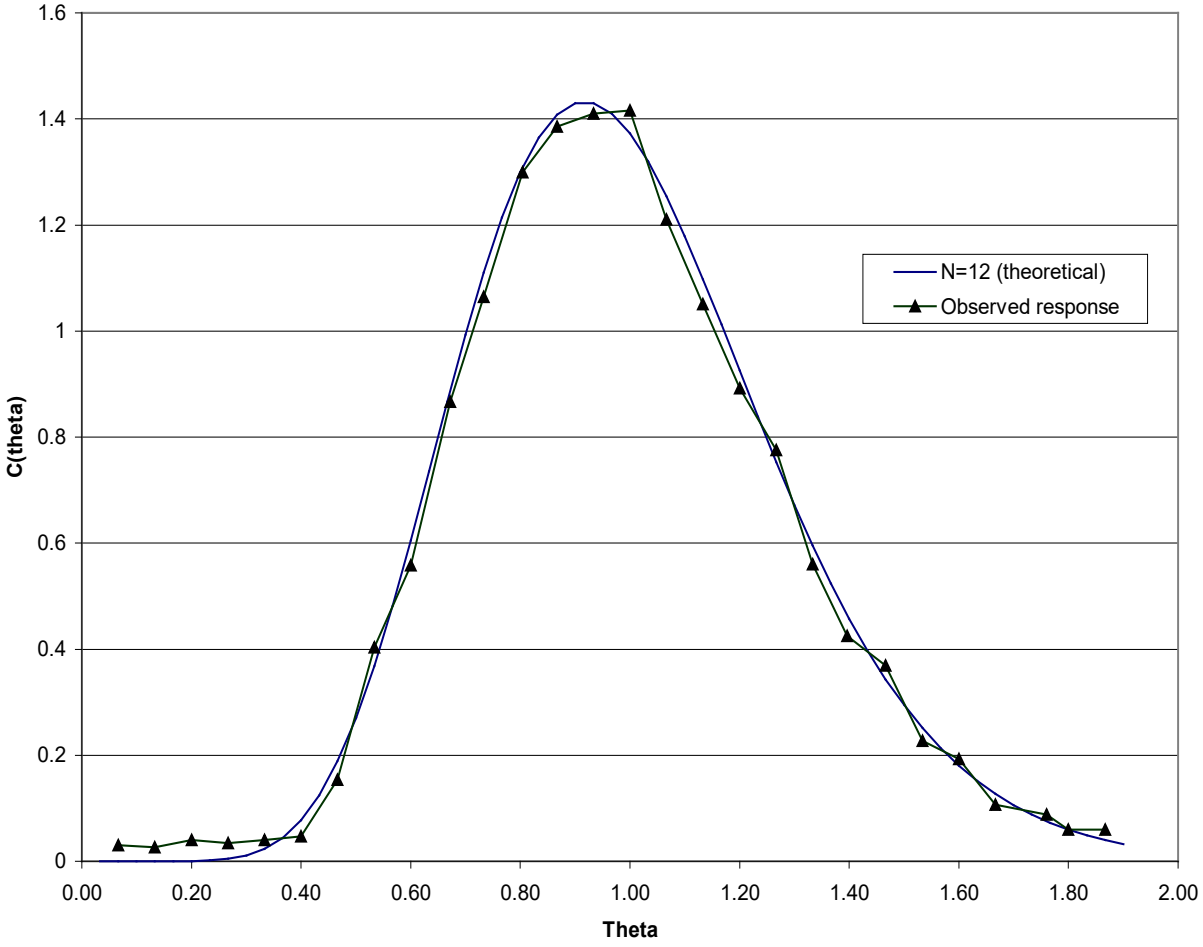
15	1,26	1,00	1,43	37,76
16	1,08	1,07	1,21	32,27
17	0,93	1,13	1,05	28,03
18	0,79	1,20	0,89	23,79
19	0,69	1,27	0,78	20,69
20	0,50	1,33	0,56	14,93
21	0,38	1,40	0,43	11,33
22	0,33	1,47	0,37	9,84
23	0,20	1,53	0,23	6,05
24	0,17	1,60	0,19	5,15
25	0,10	1,67	0,11	2,85
26	0,08	1,76	0,09	2,34
27	0,05	1,80	0,06	1,59
28	0,05	1,87	0,06	1,60
			Total mass	394,4

To obtain the tracer response curve, $C\theta$ is plotted versus θ. Where $C\theta$ and θ are normalised concentration and time values respectively. These values are calculated as follows:

$C\theta$ = Concentration (C) and Dose concentration (C_o) = Mass of tracer injected
Dose Concentration (C_o) Reactor volume (V)

$$\theta = \frac{\text{Time (t)}}{\text{Theoretical hydraulic retention time (T)}}$$

The tracer response data is represented on the curve below:



The recovery for each time interval is calculated as the product of the measured tracer concentration in the interval, the time elapsed in the interval and the flow. (Mass = C $\times$ Δt $\times$ F). The total recovery is then determined by obtaining the sum of recoveries over all the time intervals:

$$\text{Tracer recovered} = \frac{\text{Sum of recoveries}}{\text{Mass of tracer injected}} = \frac{394{,}4\text{g}}{400\text{g}} = 98{,}6\% \text{ .}$$

To obtain the number of theoretical CSTR's equivalent to the CCT, the maximum value of Cθ, (Cθ_{max}), is used together with the following equation and solving for N:

$$C_{\theta_{\max}} = \frac{N(N-1)^{N-1}}{(N-1)!} e^{-(N-1)}$$

From table A2 $C\theta_{max}$ is equal to 1,43 which corresponds to N=12.

Step 2:

Determine the required survival ratio (N_e/N_i):

$$\frac{N_e}{N_i} = \frac{\text{Count required in effluent}}{\text{Initial count}} = \frac{1}{100\ 000} = \frac{N_t}{N_0}$$

Step 3:

Use Equation 6 in Pretorius & Pretorius, (1999) to determine the apparent kinetic constant, K, required to obtain the desired inactivation (survival ratio):

$$\frac{N_t}{N_o} = \left(\frac{1}{1+K\tau'}\right)^N \cdot \sum_{i=0}^{j-1} \left[\frac{i+N-1}{N-1}\right]\left(\frac{K\tau'}{1+K\tau'}\right)^i$$ (Equation 6, Pretorius & Pretorius, (1999))

Use the best fit value of j=2 as obtained in the experimental work reported in Pretorius & Pretorius, (1999) (this may vary from one effluent to another). The value of τ' is obtained by deviding the theoretical retention time of the CCT by the N value obtained in Step 1 (N=12). Thus τ' = 1,25 min.

Substitute the values of τ' (1,25 min), N (12) and the survival ratio, N_t/N_o (0,0001), and calculate the corresponding value of K. The K value obtained in this way is 1,34 min^{-1}.

Step 4:

Use the K value obtained in Step 3 (1,34 min^{-1}) and evaluate the monochloramine concentration required at the relevant pH (pH7) from figure 3 in Pretorius & Pretorius, (1999). At this K value and pH, a monochloramine concentration of 4,2 mg/l is required to achieve the desired inactivation of feacal colifroms.

References

AIETA EM, BERG JD, ROBERTS PV and COOPER RC (1980) Comparison of chlorine dioxide in wastewater disinfection. *Journal of the Water Pollution Control Federation,* 52(4) 810-822.

AMERICAN SOCIETY OF CIVIL ENGINEERS (ASCE) (1986) Chloramines a better way?. *Civil Engineering,* 56(4) 50-51.

APHA (1989) Standard Methods for The Examination of Water and Waste Water. 17th Ed.

BERMAN D, SULLIVAN R and HURST CJ (1992) Effect of the method of preparing monochloramine upon the inactivation of MS2 coliphage, *Eschirichia coli* and *Klebsiella pneumoniae. Canadian Journal of Microbiology* 38(1) 28-33.

CARNIMEO D, CONTINI E, DI MARINO R, DONADIO F, LIBERTI L and RANIERI E (1994) Wastewater disinfection by UV at Trani municipal plant. *Water Science and Technology* 30(4) 125-132.

CHICK HE (1908) An investigation of the laws of disinfection. *Journal of Hygiene* 8 92-158.

DICE JC (1985) Denver's seven decades of experience with chloramination. *Journal of the American Water Works Association* 77(1) 34-37.

GRIFFIN AE and CHAMBERLIN NS (1941) Some Chemical Aspects of Breakpoint Chlorination *J NEWWA 55,* 371

HAAS CN, JOFFE J, HEATH M, JACANGELO J and ANMANGANDLA U (1998) Predicting disinfection performance in continuous flow systems from batch inactivation studies. *Proceedings of the Nineteenth Biennial Conference of the International Association on Water Quality, Vancouver, Canada, June 21 - 26.*

HOM LW (1972) Kinetics of chlorine disinfection of an ecosystem. *Journal of the Sanitary Engineering Division ASCE* 98 (SA1) 183-194.

JACANGELO JG, PATANIA NL, REAGAN KM, AIETA EM, KRASNER SW and McGUIRE MJ (1989) Ozonation: Assessing its role in the formation and control of disinfection by-products. *Journal of the American Water Works Association* August.

JOHNSON JD and JENSEN JN (1986) THM and TOX formation: Routes, rates and precursors. *Journal of the American Water Works Association* 78(4) 156-162.

KOUAME Y and HAAS CN (1991) Inactivation of *E. Coli* by combined action of free chlorine and monochloramine. *Water Research* 25(9) 1027-1032.

KREFT P, UMPHRES M, HAND JM, TATE C, McGUIRE MJ and TRUSSEL RR (1985) Converting from chlorine to chloramines: a case study. *Journal of the American Water Works Association* 77(1) 38-45.

LEVENSPIEL O (1972) Chemical Reaction Engineering. *John Wiley & Sons, New York.*

MASTERTON LM, SLOWINSKI EL, STANITSKI CL (1985) Chemical Principles 6th Ed. *Holt-Saunders International, Philadelphia.*

PALIN AT (1974) Chemistry of modern water chlorination. *Water Services* 78 (935).

PRETORIUS WA and PRETORIUS PC (1999) Disinfection of purified sewage effluent with monochloramine. *Water SA,* 25(4) 463 – 471.

REYNOLDS G, MEKRAS C, PERRY R and GRAHAM N (1989) Alternative disinfectant chemicals for trihalomethane control - A review. *Environmental Technology Letters* 10 591- 600.

RICE EW, COVERT TC, WILD DK and BERMAN D (1993) Comparative resistance of *Escherichia Coli* and enterococci to chlorination. *Journal of Environmental Science and Health* A28(1) 89-97.

SEVERIN BF, SUIDAN MT and ENGELBRECHT RS (1984) Series-event kinetic model for chemical disinfection. *Journal of Environmental Engineering* 110(2) 430-439.

SHULL KE (1981) Experience with chloramines as primary disinfectants. *Journal of the American Water Works Association* 73(2) 101-104.

SMITH JM (1981) Chemical Engineering Kinetics. *McGraw-Hill, New York.*

TEEFY SM and SINGER PC (1990) Performance and analysis of tracer tests to determine compliance of a disinfection scheme with the SWTR. *Journal of the American Water Works Association* 82(12) 88-98.

WARD NR, WOLFE RL AND OLSON B (1984) Effect of pH, application technique, and chlorine-to-nitrogen ration on disinfectant activity of inorganic chloramines with pure culture bacteria. *Applied and Environmental Microbiology* 48(3) 508-514.

WATSON HE (1908) A note on the variation of the rate of disinfection with change in the concentration of the disinfectant. *Journal of Hygiene* 8 536-592.

WHITE GC (1992), *Handbook of Chlorination and Alternative Disinfectants,* New York: Van Nostrand.

WHITE GC AND BEEBE RD (1983) *Problems of Disinfecting Nitrified Effluents",* Municipal Wastewater Disinfection, Proc. of Second Ann. Nat. Symposium, Orlando, FL, EPA Report 600/9-83-009, July 1983.

YAMAMOTO K, FUKUSHIMA M and ODA K (1988) Disappearance rates of chloramines in river water. *Water Research* 22(1) 79-84.

APPENDIX A

Findings of the National Disinfection Survey

1. Process Type and Capacity

The chart below (Figure A) shows the different process types employed at the sewage treatment plants surveyed. The percentages shown was calculated based on the wastewater flow treated per day. It was found that the major proportion of the daily flow (89%) was treated with an activated sludge process, either alone or in combination with biofilters.

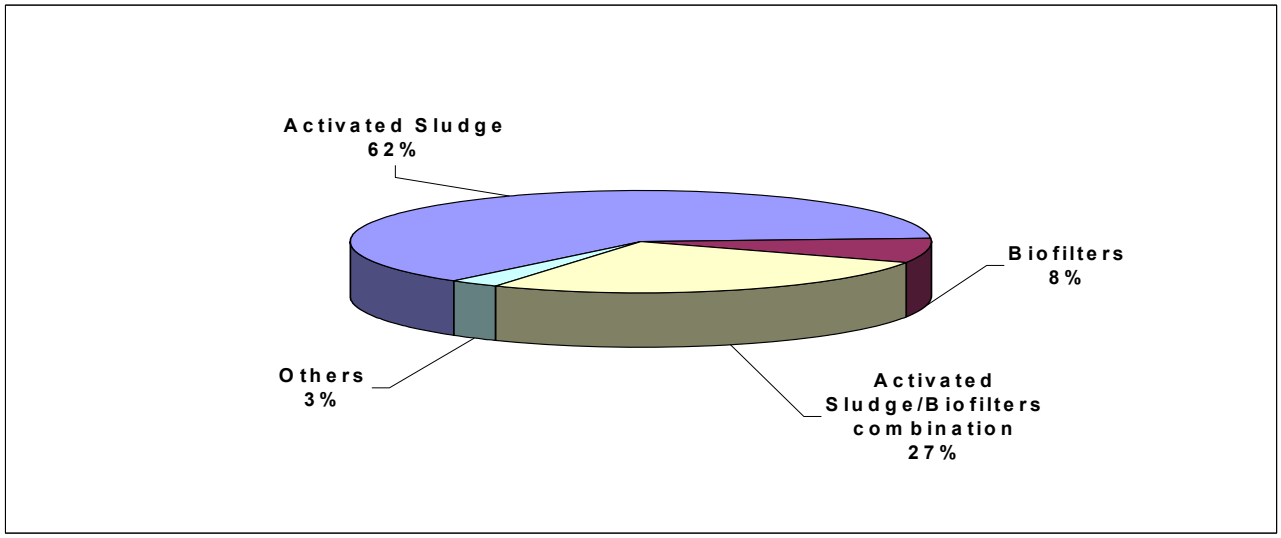


Figure A: Distribution of process type based on percentage of daily treated flow.

The treatment capacities of the plants surveyed varied over a wide range as shown in Figure B. The percentages presented here are based on the design capacities of the plants in Ml/day.

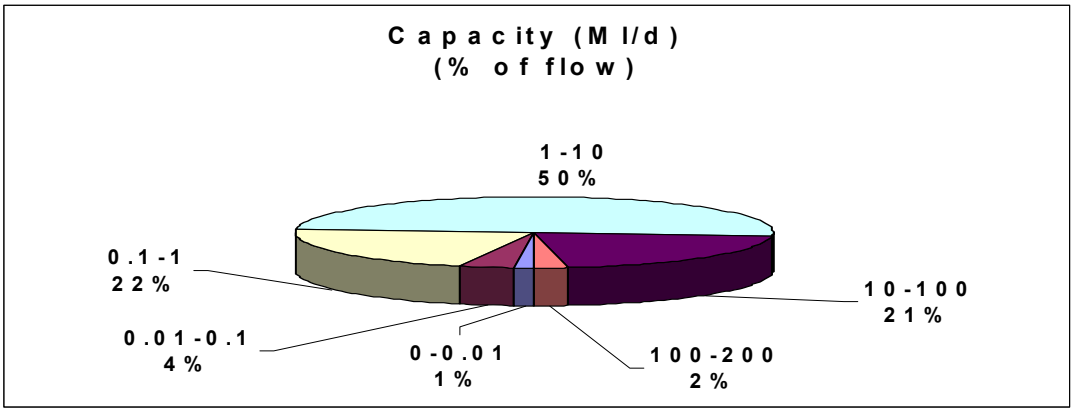


Figure B: Distribution of the design capacities of the plants surveyed.

2. Disinfection Practices

The survey revealed that 21% of the total flow was not disinfected at all. Chlorine was found to be the most widely used disinfectant, either alone or in combination with bromine (Figure C).

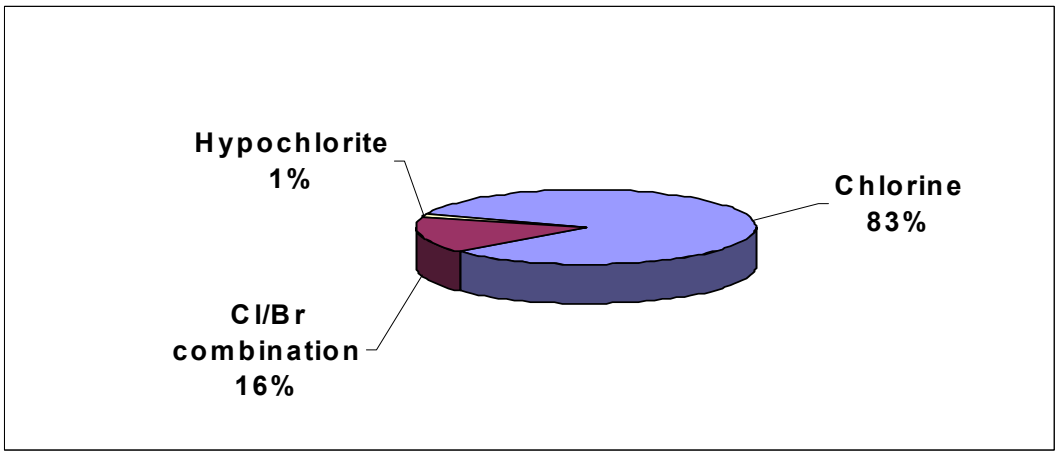


Figure C: Disinfectant used by the plants surveyed based on total daily flow.

The average chlorine dosage applied varied between less than 1mg/l to more than 8mg/l. The complete distribution of dosages applied is shown in (Figure D).

2.3. Effluent Quality and the Receiving Environment

The survey included both coastal and inland plants discharging their effluent to the ocean, public streams and dams. The majority of effluent is discharged to public streams (see Figure E). This statistic is very significant if the bacteriological quality of the effluent is considered. Only 33% of the effluent discharged achieved *E. Coli* counts of Nil CFU/100ml. The effluent quality of the plants surveyed appears in Figure F .

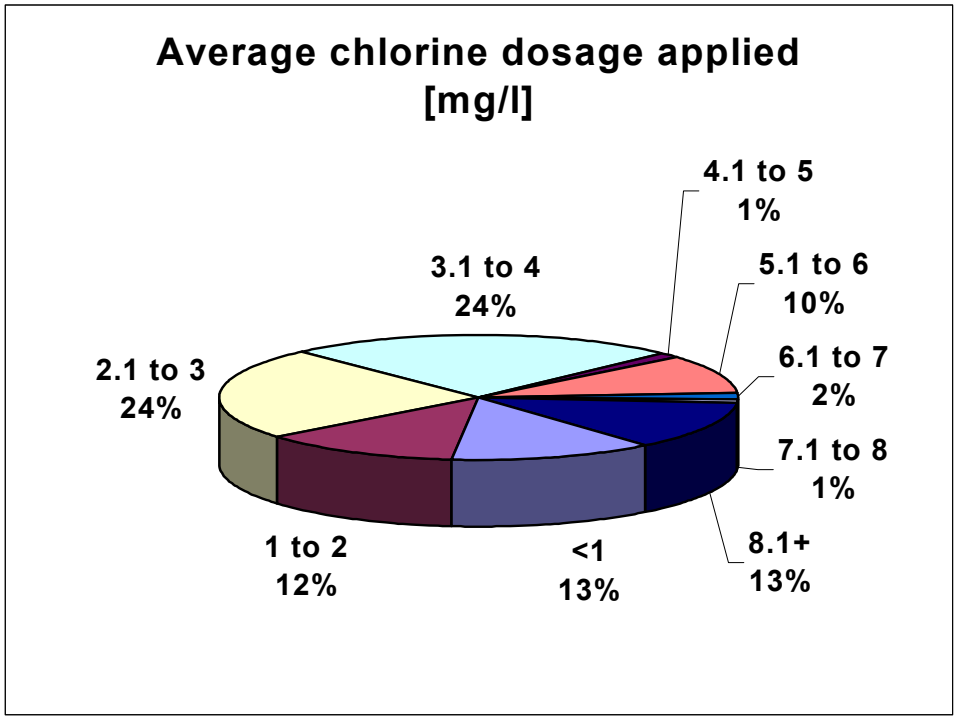


Figure D: Distribution of chlorine dosages applied based on total daily flow

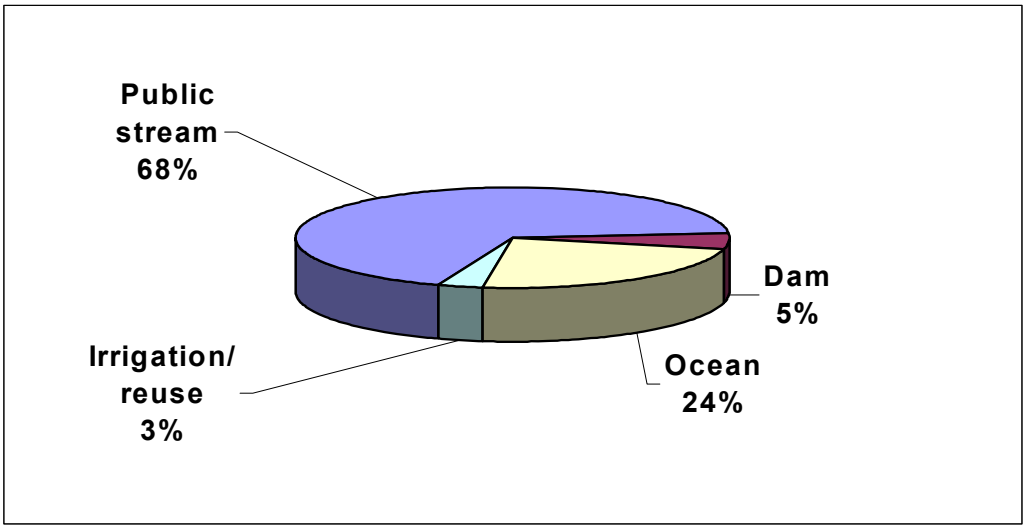


Figure E: Water bodies receiving the final effluents of the plants surveyed.

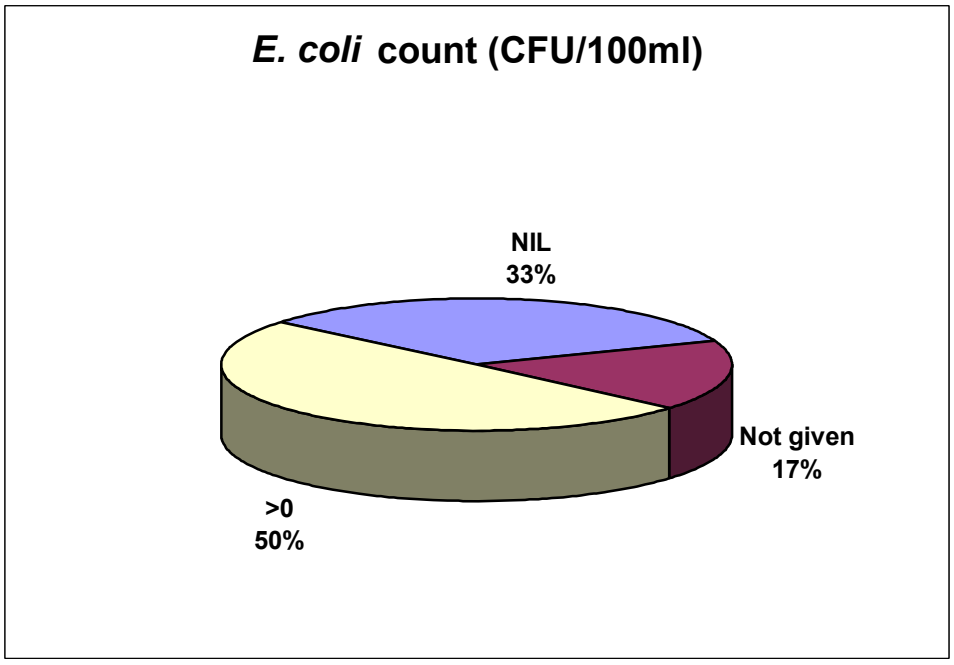


Figure F: Bacteriological quality of the effluent.

2.4. Details of Disinfection Facilities

Of the plants surveyed, 25% reported that no dedicated contact basin was available for disinfection. The majority of plants that did have contact basins, reported that these basins were open (88%). The most prevalent design found was a square baffled basin (see Figure G). Theoretical retention times varied between less than 20 minutes to more than 240 minutes (see Figure H) with the majority in the 20 to 45 minute category. 91% of the plants that practice disinfection controlled the process by taking samples, doing bacterial counts and adjusting the disinfectant dosage to ensure acceptable effluent quality. None of the plants used flow paced dosing i.e. disinfectant is applied at a constant rate independent of the flow rate.

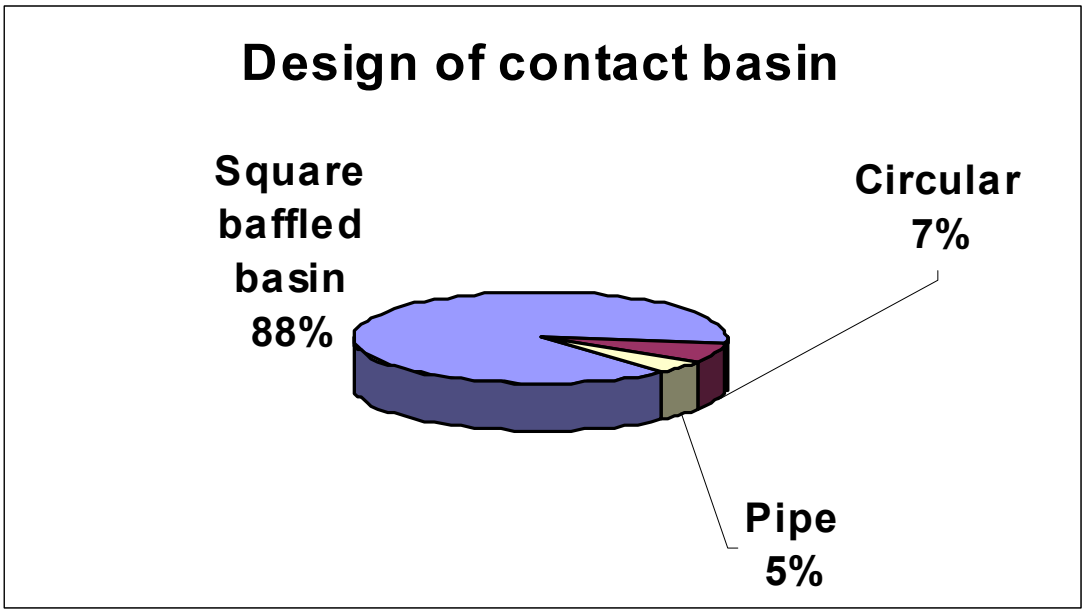


Figure G: Prevalence of different contact basin designs.

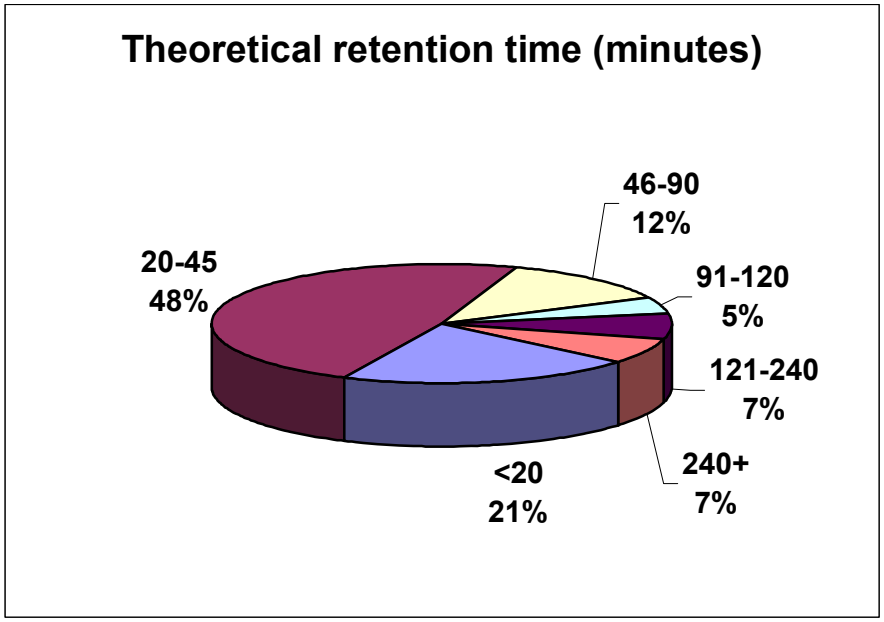


Figure H: Distribution of theoretical retention times in contact basins.

2.5. Summary

- 175 Works returned questionnaires.
- A total flow of 2 million cubic meters of water is treated per day.
- Approximately 5,7 tons of chlorine gas is consumed by 130 works per day.
- Activated sludge, alone and in combination with biofilters, is the predominant treatment process (89% of respondents).
- Most effluent is discharged to public streams (68%) and the ocean (24%).

- 21% of the flow is not disinfected.
- Chlorine is the dominant disinfectant (83% of disinfected flow).
- Most common dosage is 1-4mg/l.
- Only 33% of the total effluent flow comply with bacteriological standards.
- 25% of works have no dedicated contact basin.
- Majority of works have open, square baffled basins (80%+)
- 81% of basins have a contact time of less than 90 minutes.

Appendix B: Disinfection of purified sewage effluent with monochloramine

PC Pretorius and WA Pretorius

Division of Water Utilisation Engineering, Department of Chemical and Environmental Engineering, University of Pretoria, Pretoria 0002

Abstract

The inactivation of fecal coliforms in purified sewage effluent by monochloramine was investigated using batch tests. For comparative purposes the data obtained were fitted to various published disinfection models. The series-event kinetic model was found to be the most suitable and was used in conjunction with tracer experiments to compare the predicted and observed inactivation of fecal coliforms in two continuous-flow systems. The value for the apparent kinetic constant K, was found to vary between 0,23 and 2,18min^{-1} for monochloramine concentrations in the 1 to 5mg/l range and pH values between 6 and 8. The model was able to predict the behaviour of the continuous-flow systems. A design example for the determination of the monochloramine concentration required for a specific inactivation of fecal coliforms in an existing contact tank is given.

Background

The South African General and Special Standards stipulate that treated sewage effluent should comply to a standard of nil fecal coliforms/100ml (Act 96 of 18May 1984 No9225, Regulation 991). This standard can only be achieved by disinfection. Various methods of disinfection are available including physical (e.g. ultraviolet radiation) (Carnimeo, *et. al.,* 1994) and chemical processes (e.g. chlorine, bromine and ozone) (Aieta, *et. al,* 1980; Jacangelo, *et. al.,* 1989). According to White (1992) the most prevalent practice of disinfection is free chlorine ($HOCl + OCl^-$). This is also the practice in South Africa as was confirmed by a recent survey (Unpublished data, Univ. of Pretoria, 1996). Chlorine is a very reactive chemical and does not only disinfect, but also rapidly reacts with contaminants such as NH_4^+, NO_2^-, H_2S, Fe^{++}, Mn^{++} and organic compounds (Yamamoto, *et al.*, 1988; Teefy & Singer, 1990). These compounds create a chlorine demand so that chlorine is applied until the demand is met and free chlorine appears. This practice is called breakpoint chlorination and is wasteful in that it consumes

more chlorine than is required for disinfection alone. The reaction of free chlorine with certain organic compounds present in wastewater leads to the formation of a group of compounds called trihalomethanes (THMs) (Johnson and Jensen, 1986), which have associated health risks (Reynolds, *et al.*, 1989). This is a concern in South Africa where treated sewage effluent is often reused as drinking water.

Some of the problems associated with free chlorine can be overcome by using chloramines for disinfection. Benefits of using chloramines include a reduction in the formation of THMs as reported by Reynolds, *et al.,* (1989) and greater disinfectant stability resulting in a reduction in disinfectant demand. Disadvantages of chloramines are their relatively long lifetime (compared to free chlorine) after discharge to the receiving environment, possibly with toxicity problems (Yamamoto, *et al.*, 1988) and their detrimental effect on kidney dialysis patients (Kreft, *et. al.,* 1985).

The chloramines are formed by the reaction of free chlorine with ammonia. The reaction produces three main compounds, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine or nitrogen trichloride (NCl_3). Palin (1974) showed that the dominant species formed in the reaction is dependent on the chlorine to nitrogen mass ratio (Cl_2:N). A low ratio (up to 5:1) favours the formation of NH_2Cl and higher ratios (up to 7,6:1) favour the formation of $NHCl_2$ and NCl_3. Ward *et al.,* (1984), found that the three species also vary in their disinfectant power, with monochloramine being less effective than dichloramine. Studies have shown that free chlorine is a more effective disinfectant than the chloramines (Berman *et al.*, 1992; Kouame & Haas, 1991; Rice *et al.*, 1993; Ward *et al.*, 1984) while some field reports (that observe naturally occurring bacteria and water with a chlorine demand) have shown that chloramines are adequate, and in some cases superior to free chlorine in terms of indicator organism reductions (Dice, 1985; Shull, 1981; Reynolds *et al.*, 1989; ASCE, 1986).

Disinfection with chlorine and chloramines is influenced by five major factors, i.e. initial indicator organism concentration, disinfectant concentration, contact time, temperature and pH. Batch inactivation studies, performed in the laboratory to observe the efficiency of a disinfectant, are usually

performed with pure culture bacteria, distilled water and well defined contact times (Ward *et al.*, 1984). This is not the case in practice, where a complex mixture of bacteria and chemical species are present, and the contact time is dependant on the mixing regime (Teefy & Singer, 1990). The design of a full-scale disinfection process would be enhanced if the results of batch inactivation studies performed on real sewage effluents in the laboratory could be matched with the hydraulic behaviour of a real continuous-flow contact chamber.

The aim of this work was to evaluate the disinfection efficacy of monochloramine under operational conditions and to show how this information may be used in the design calculations of a chloramine disinfection system.

Theoretical

Kinetic models for batch inactivation

Since the turn of the century various mathematical models have been developed to describe the inactivating action of a disinfectant on micro-organisms. The main inactivation models found in the literature are summarised in Table 1.

Table 1: Summary of the principle inactivation models.

Model	Eq.	Author	Comments
$\ln \frac{N_t}{N_o} = -kC^n t$	(1)	Chick/Watson (1908)	First-order with respect to surviving bacteria if C is constant. k is the pseudo first-order reaction rate constant and n is the coefficient of dilution.

$\ln\frac{N_t}{N_o} = -kC^n t^m$	(2)	Hom (1972)	Model developed to account for deviations from the Chick-Watson model in practice. m is an empirical constant and k and n are as for Eq. (1
$\ln\ \frac{N_t}{N_o} = -k't^m$	(3)	Hom (1972)	Modification of Eq. (2) for constant disinfectant concentration. $k' = kC^m$ in Eq. (2).
$\frac{N_t}{N_o} = e^{-kct}\sum_{i=0}^{j-1}\frac{(kct)^i}{i!}$	(4)	Severin (1984)	The series event kinetic model where is the mixed second-order reaction rat constant and j is an integer represent-ing the lethal number of reactions for a single organism. The term kC may be replaced by K, the apparent kinetic constant
$\ln\frac{N_t}{N_o} = -\left(\frac{m}{nk^*}\right)^m k(C_o)^n\left[1-\exp\left(-\frac{nk^*t}{m}\right)\right]^m$	(5)	Haas *et al. (*1998)	A modification of the Hom model developed to take residual disinfectan decay into account. k, m and n are the same as for Eq. (2). C_o is the initial disinfectant concentration and k* the first-order residual decay rate.

N_o = initial concentration of organisms
N_t = organism concentration at time t
C = disinfectant concentration
k = reaction rate constant
m = empirical constant
n = coefficient of dilution
k^* = first-order residual decay rate
j = lethal number of reactions

Because the recent models (Eqs. (4) and (5)) are more complex than the older ones (Eqs. (1) (2) and (3)), all the models were compared to determine which one gave the best prediction of the kinetics for

batch inactivation studies and to determine whether the more complex models are more accurate than the older models. The rationale was to identify a model that is both accurate and simple.

Continuous flow residence time distribution models

Not all the elements of a fluid pass through a reactor along the same flow path and some short-circuiting may take place. This creates a distribution in the residence time as shown by Levenspiel (1972: 255) of the different fluid elements, called the residence time distribution (RTD) . Tracers are used to measure the RTD of a reactor. The tracer is injected at the influent to the reactor and measured as it exits . The resulting response curve may then by analysed by means of mathematical models. Three models are available for this analysis: the tanks-in-series model, the dispersion index model and indices calculated from single points on the response curve.

The tanks-in-series model assumes that the flow through a real reactor may be represented as though it flows through a series of equally sized completely stirred tank reactors (CSTRs) (Levenspiel, 1972: 290). The number of CSTRs, N, is obtained by comparing the tracer response curve of a reactor to the theoretical response of a known number of CSTRs. Values of N range between two theoretical extremes (Smith, 1981: 283), i.e. N = 1 (a completely mixed reactor) and N = ∞ (a plugflow reactor). One of the advantages of the tanks-in-series model is that it uses all measured data and not only single points on the response curve.

The tanks-in-series model is used to evaluate tracer data obtained in this study because mathematical models already exist that combine batch disinfection data with a tanks-in-series model as shown by Severin *et al.* (1984). To combine the residence time distribution of a continuous-flow system with the results of a batch inactivation study it is necessary to write the batch model as an inactivation equation that will predict the survival ratio (N_t/N_o) of the bacteria in the effluent stream. The inactivation equation developed by Severin *et al.* (1984): for the series-event model was used in this study and is given below:

$$\frac{N_t}{N_o} = \left(\frac{1}{1+K\tau'}\right)^N \cdot \sum_{i=0}^{j-1} \left[\frac{i+N-1}{N-1}\right]\left(\frac{K\tau'}{1+K\tau'}\right)^i \qquad (6)$$

Where K = apparent kinetic constant (min^{-1})

τ' = residence time in one CSTR

N = number of equally sized CSTRs in series

N_o = initial concentration of organism

N_t = concentration of organism at time t (min).

The value of τ' and N can be obtained from tracer studies while the value of K and j can be obtained from batch inactivation experiments.

The experimental work done in this study can be summarised as follows:

- Batch inactivation experiments were conducted with treated sewage effluent to determine the effect of pH and monochloramine concentration on the inactivation rate of naturally occurring fecal coliforms in the effluent.
- Tracer studies were conducted on two continuous-flow laboratory-scale contact chambers, namely reactors in series and a channel-flow reactor, to determine their flow regimes (number of CSTRs in series, N).
- The data obtained in the batch inactivation experiments were fitted to mathematical models to identify the most accurate model.
- The data measured in the batch inactivation experiments and tracer experiments were combined (Eq. (6)) to predict the inactivation in the two continuous-flow systems.
- Inactivation was measured in the two continuous-flow systems and was compared to the predictions of Eq. (6).

Methodology

Test Water

All the experiments were conducted on secondary treated effluent from a typical biological nutrient removal wastewater treatment plant, treating mainly domestic sewage. Samples of the effluent were collected from the secondary settling tank overflow (before disinfection) in batches and stored at 4°C within 1hr of collection. Experiments were done within 4d after collection. Thereafter the samples were discarded and new samples were collected.

Preparation of disinfectant solution

Before each set of inactivation studies a fresh stock solution of monochloramine was prepared by adding 44ml of a 5% (m/m) NaOCl solution (ACE chemicals) to 456ml of a 8,3g/l HH_4Cl solution (Merck) to produce 500ml of a NH_2Cl concentration of ca. 2g/l (Cl_2:N mass ratio = 3:1)(Ward *et al.,* 1984). The solution was stirred for 1h to allow the reaction to go to completion and was standardised by analysing the different chloramine species using the ferrous ammonium sulfate-diethyl-*p*-phenylenediamine titrimetric method (APHA, 1989).

Batch inactivation studies

To determine the effect of pH on disinfection efficiency , inactivation studies were conducted at pH 6, pH 7 and pH 8. The experiments were conducted in the monochloramine concentration range of 1 to 5 mg/l as Cl_2 . The actual monochloramine concentration present in each individual experiment varied within this range and was dependant upon the standardised concentration of the stock solution and the volume that could accurately be dispensed. All inactivation studies were conducted in batch experiments at 25°C±1°C in sterile 1ℓ glass sample bottles. Test water was placed in the sample bottle and the pH was adjusted to the required value using a concentrated phosphate buffer solution (yielding a final concentration of ca. 20mM) and a digital pH meter (Metler-Toledo MP120). Once 25°C and the

required pH was reached a sample was taken to establish the original fecal coliform count (N_o). The monochloramine was added to the test water from the pre-prepared stock solution to obtain the relevant residual concentration. After addition of the monochloramine the pH of the solution was measured to ensure that the test was done at the correct pH. While continuously stirring the solution, 5ml samples were removed at pre-selected contact times (between 2 and 40 min depending on the inactivation rate) and combined with 5ml of a sterilised thiosulfate solution of sufficient strength to neutralise the monochloramine residual as reported by Ward *et. al.* (1984). After dilution the surviving fecal coliform bacteria were counted taking into account the dilution of the neutralising thiosulphate solution.

Inactivation in continuous-flow systems

To extend the batch inactivation studies to continuous-flow systems, two bench-scale chlorine contact tanks (CCT) were constructed from Plexiglas. The first CCT consists of 8 identical CSTRs in series and the second CCT was a narrow channel with a small initial mixing chamber. Figures 1 and 2 show schematic diagrams of each CCT. These two CCT configurations were chosen to correlate mixing data (from tracer studies) and observed bacterial inactivation with inactivation predicted from the batch inactivation studies. Inactivation studies were conducted in each CCT by feeding test water and monochloramine solution at a constant rate and allowing the system to reach steady state by passing three reactor volumes of feed through the reactor. After steady state was reached in Reactor 1, bacterial samples were taken of the feed water as well as in each of the eight cells. In Reactor 2 samples of the feed and the reactor effluent were taken and analysed for fecal coliform numbers. The operating conditions and results of this experiment are shown in Table 3.

Enumeration of bacteria

The test organism used was the fecal coliform group as specified by the South African Bureau of Standards. Enumeration of bacteria was conducted using the membrane filter technique; method 9222D (APHA, 1989). Samples were diluted into decimal dilution series using sterilised water. Appropriate volumes of water were passed through sterile 0,45-μm pore-size cellulose nitrate filters (Whatman WCN type) and washed with sterilised wash water. The membranes were removed and

placed on commercial m-FC agar media (Merck Biolab medium C29) for the enumeration of fecal coliforms. All colonies with a blue colour were counted after incubation at 44°C for 24h and bacterial concentrations in the original samples were calculated.

Tracer studies

The mixing regime in each CCT was determined by conducting tracer studies with lithium as tracer. All tracer experiments were done as pulse inputs. The constant flow in each reactor was adjusted to reflect the flow rate used in the continuous flow inactivation studies. Samples were taken of the reactor effluent at constant time intervals of one minute and analysed with an atomic absorption spectrophotometer (Varian AA-1275, Air-Acetylene).

Data analysis

To find the most accurate model for batch inactivation kinetics, the data obtained from the batch inactivation studies were fitted to Eqs. (1), (3), (4) and (5) (Eq. (1) showed significant deviation from the observed data and no further attempt was made to use this equation). Equation (3) was linearized and fitted with Microsoft Excel 97 software (Microsoft corporation, California, 1993) using linear regression. Equation (4) was fitted using a spreadsheet to obtain the best fit value of j for a set of experiments conducted at a specific pH. This was done by evaluating the least sum of squares of deviation of the observed data to the predictions of Eq. (4). The least square best fit value of K was then recorded (Severin, *et al.,* 1984). Equation (5) was fitted with DataFit software (Oakdale Engineering, USA) using non-linear regression analysis and the best fit values of k, m and n were recorded for each of the experiments. The accuracy of each model was then evaluated by comparing the correlation coefficients (R^2) calculated for each model.

The following method was used to predict the survival ratios of bacteria in the effluent streams of the CCTs:

- The series-event model for a number of CSTRs in series (Eq. 6) was used (Severin et al., 1984)
- The value of K was graphically evaluated from Fig. 3 at the monochloramine concentration and pH at which the experiment was conducted.
- The best fit value of j=2 was used as reported in Table 2.
- The N value for each reactor, as obtained from the tracer experiment, was used in Eq. (6).

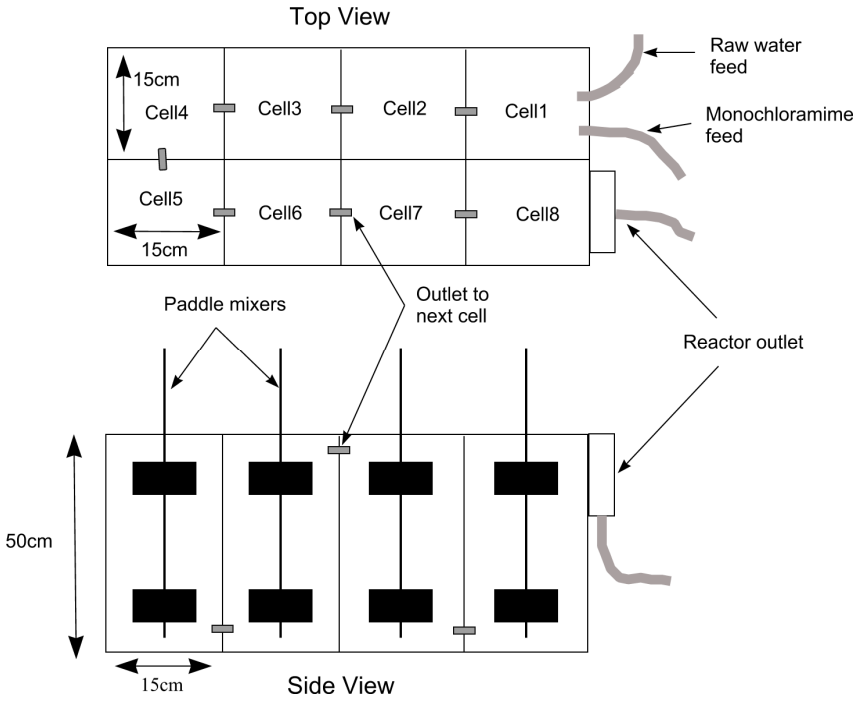


Figure 1: CSTRs in series (Reactor 1)

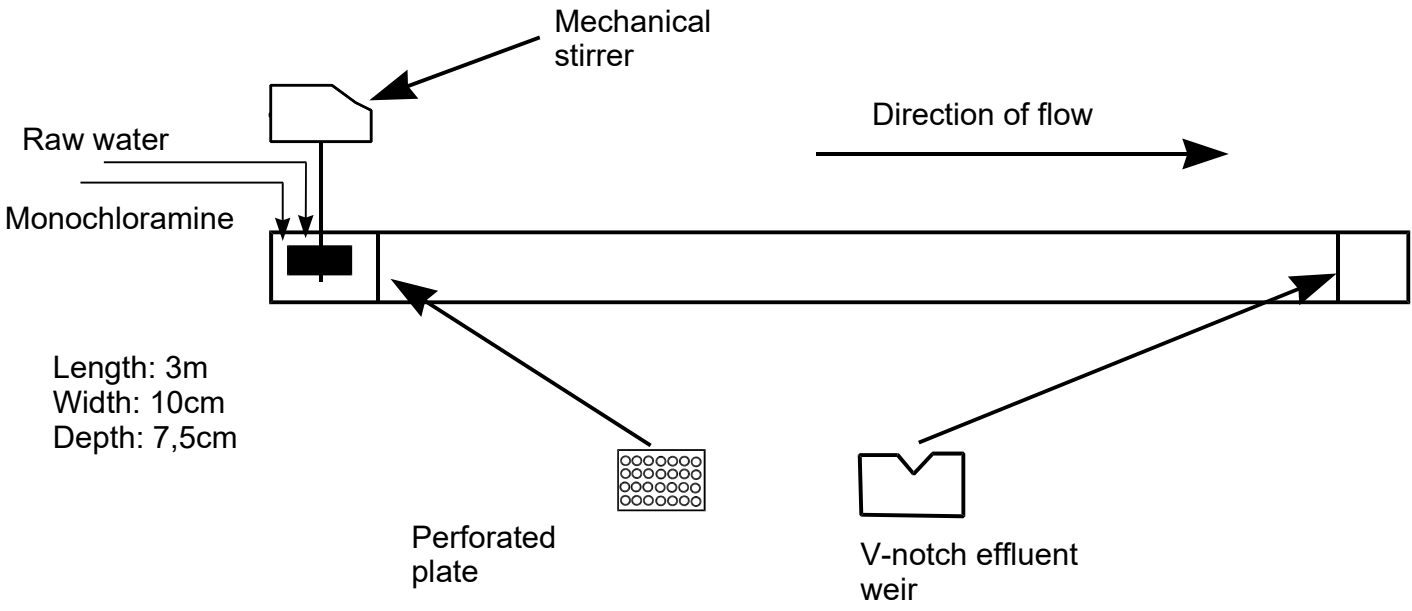


Figure 2: Channel (Reactor 2)

Results and discussion

Batch inactivation studies

The fitted parameters and correlation coefficients (R^2) for each of the models evaluated are given in Table 2. Referring to Table 2, there are 5, 11 and 8 sets of data that can be fitted to Eqs. (3), (4) and (5) respectively with a correlation coefficient greater than 0,95. Equation (4) was not only found to be the model that best represented the experimental data, but also gave values for the apparent kinetic constant, K, that increased with an increase in monochloramine concentration and increased with decreasing pH as would be expected (see comparison with study by Ward *et al.* (1984)). The values of the kinetic reaction coefficients of the other two equations show a more random variation making it difficult to use them to predict disinfection efficiency. The relationship between K (Eq. (6)) and monochloramine concentration is shown in Fig. 3.

Table 2: Comparison of the correlation of different kinetic models for batch inactivation studies.

Exp No.	$[NH_2Cl]$ mg/l	Equation (3)			Equation (4)			Equation (5)			
		k'	m	R^2	j	K	R^2	k	m	n	R^2
1	1.4	0.281	0.928	0.981	2	0.305	0.963	0.036	1.859	0.139	0.972
2	2.4	0.361	0.715	0.845	2	0.883	0.932	0.055	2.613	0.584	0.973
3	3.4	2.188	0.455	0.874	2	1.186	0.999	ND	ND	ND	ND
4	4.4	0.158	2.405	0.898	2	2.180	1.000	ND	ND	ND	ND
5	1.0	0.062	1.303	0.907	2	0.238	0.989	0.000	5.199	0.698	0.995
6	1.7	0.029	1.774	0.884	2	0.417	0.986	0.002	5.183	1.317	0.980
7	2.4	0.462	0.943	0.890	2	1.180	0.998	0.179	1.108	0.113	0.993
8	3.3	0.547	1.230	0.928	2	1.337	0.999	0.218	1.793	0.593	0.905
9	4.6	1.714	0.678	0.994	2	0.318	0.943	0.038	1.628	0.055	1.000
10	1.2	0.065	1.282	0.961	2	0.562	0.973	0.129	1.450	0.144	0.996
11	2.5	0.081	1.475	0.950	2	1.137	1.000	0.119	2.412	0.601	0.947
12	3.8	0.782	0.798	0.965	2	2.14	1.000	0.412	1.117	0.220	0.974
13	4.7	6.383	0.744	0.746	2	0.952	0.982	ND	ND	ND	ND

ND = Could not be fitted to model due to insufficient number of data points on inactivation curve.

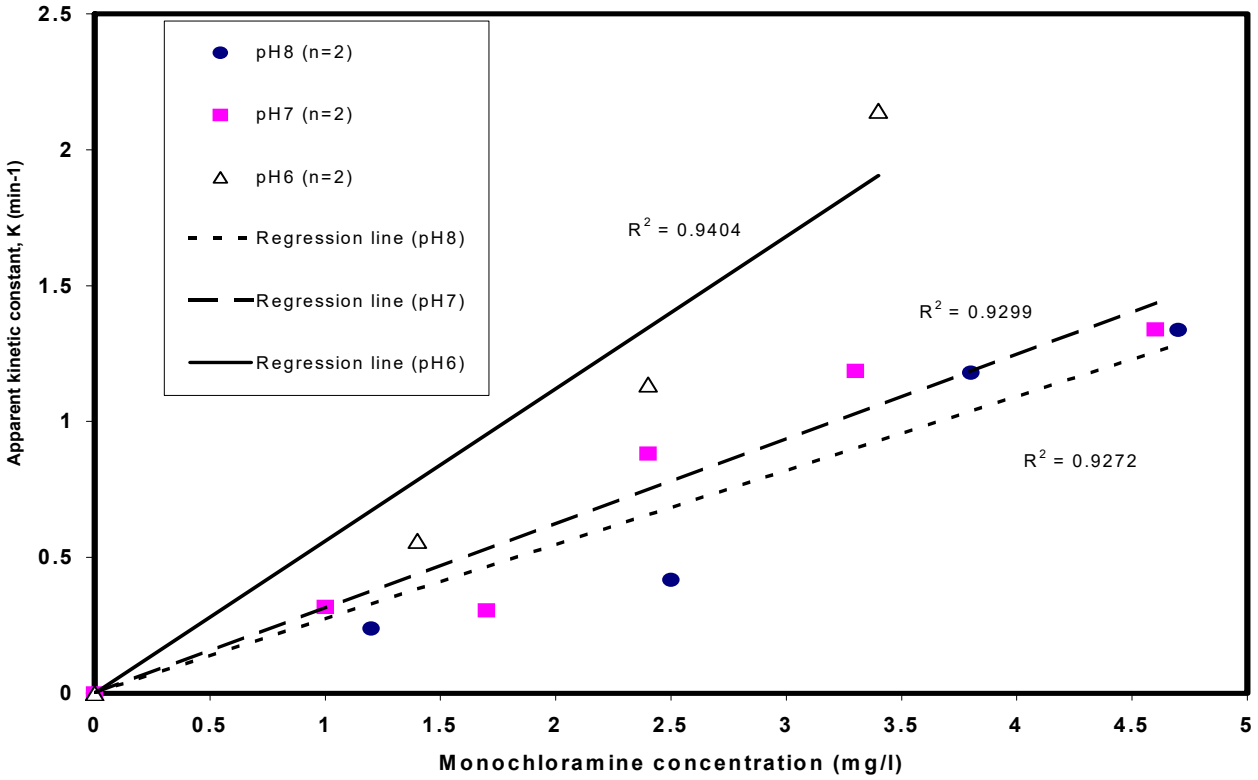


Figure 3: The relationship between the apparent kinetic constant (K) and monochloramine concentration as measured at different pH values in batch experiments.

The relationship between monochloramine concentration and the time required to effect a 99% reduction in fecal coliform numbers (t99) at three different pH values is shown in Fig. 4. The graph was generated using Eq. (3) to determine the t99 values. The data are presented in this way (i.e. using Eqn (3) instead of (4)) so as to compare the data obtained in this study to results obtained by other workers who presented their data in this way. A study by Ward *et al.* (1984) who used monochloramine, *E. coli* and chlorine demand-free solutions is shown on the same graph (Fig. 4) for comparison. The disinfection efficiency measured in this study compares relatively well to that measured by Ward under demand-free conditions. This indicates that the disinfectant capability of monochloramine is not significantly influenced by chlorine demand-causing materials as is the case with free chlorine. The disinfection efficiency measured in this study was less sensitive to pH than that measured by Ward (1984).

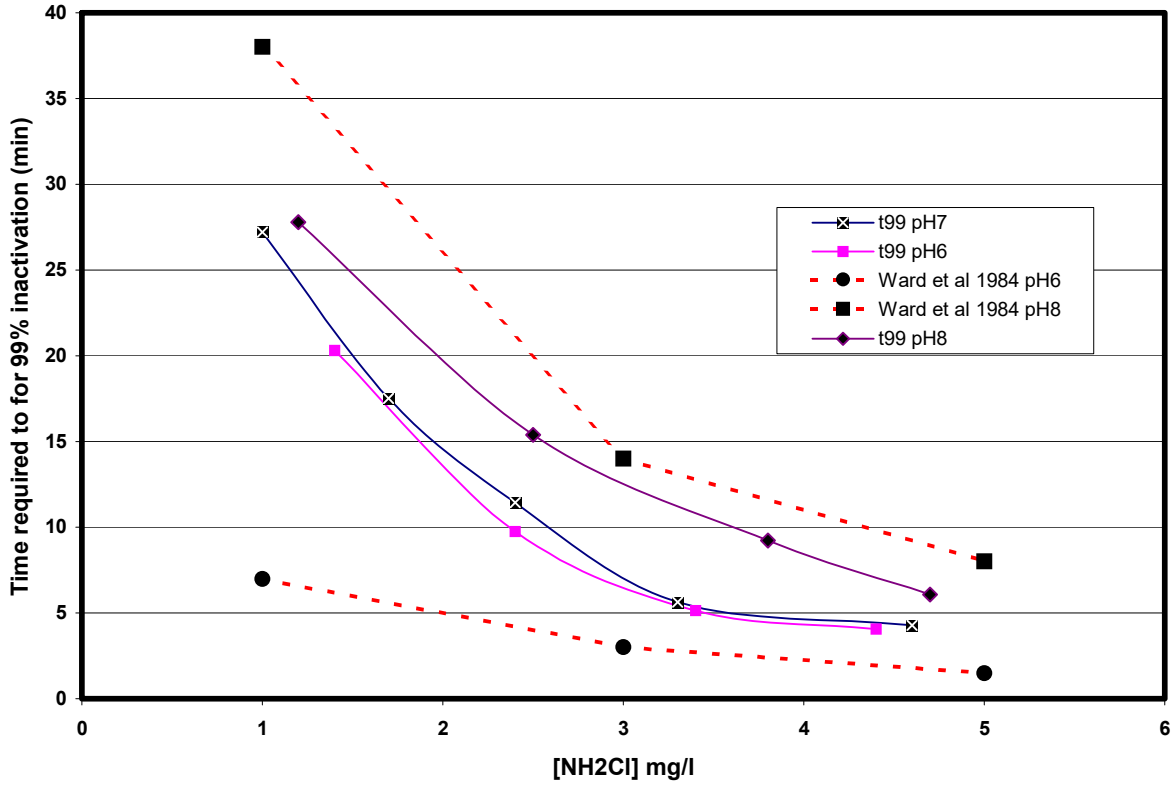
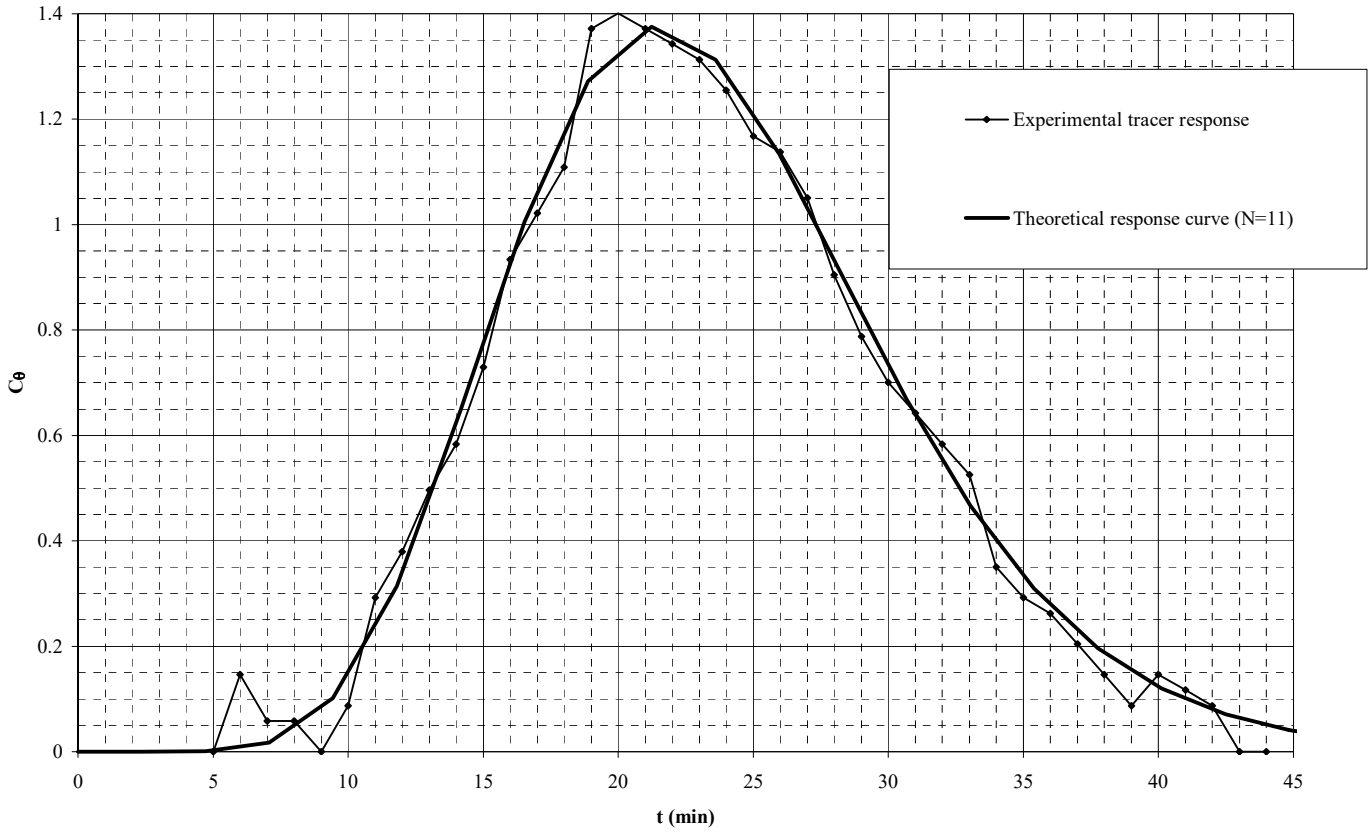


Figure 4: A comparison between the disinfection efficiency obtained in this study and that measured by Ward *et al.* (1984) at different pH values and monochloramine concentrations.

Tracer studies

The tracer response curves for each of the two CCTs are shown in Figs. 5 and 6 respectively along with the theoretical curve for the corresponding number of theoretical CSTRs (N) obtained by analysis with the tanks-in-series-model.

Figure 5: Experimental and theoretical tracer response curves for Reactor 1



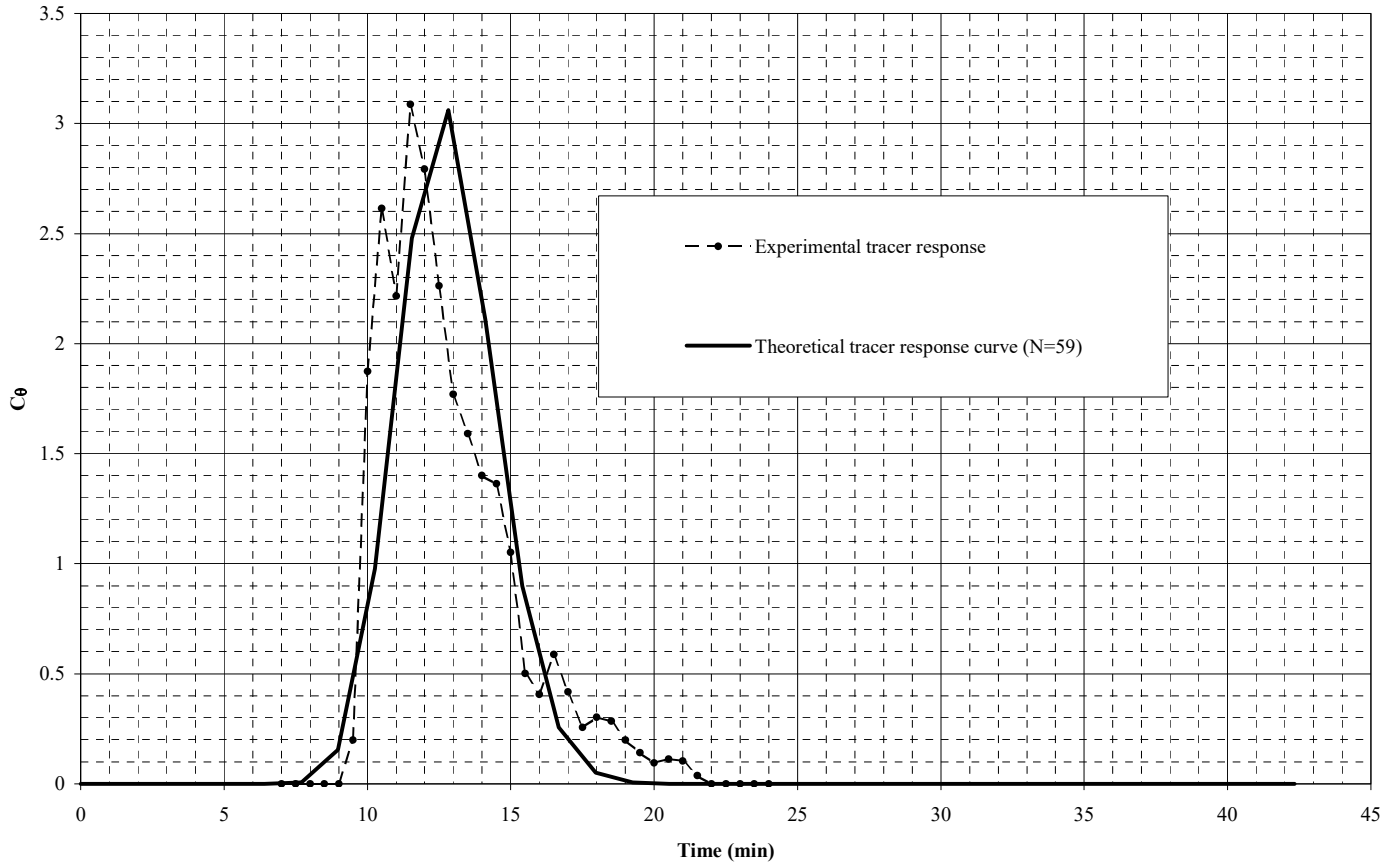


Figure 6: Theoretical and experimental tracer response curves for Reactor 2

The results show that the mixing regime in Reactor 1 corresponds to that of 11 CSTRs in series (N=11), while the mixing regime in Reactor 2 approaches plugflow conditions (N=59).

Inactivation in continuous flow systems

The inactivation of fecal coliforms as measured in the continuous flow CCTs are summarised in Table 3 along with the predicted survival ratios as calculated by means of Eq. (6). Survival ratios for Reactor 1 were predicted (Eq. 6) for each cell in the reactor. (The tracer study showed that the reactor was equivalent to 11 theoretical CSTRs. It was therefore assumed that each of the 8 physical cells was equivalent to 11/8 theoretical CSTRs).

Table 3: Comparison between observed and predicted inactivation in the continuous flow systems

Reactor 1			pH=7,39 [NH_2Cl] =0,8 mg/l Temperature =21°C	
Sample		Nt/No (observed)		Nt/No (predicted, N=11)
Cell1		0.557		1.271 (not applicable)
Cell2		0.391		0.495
Cell3		0.313		0.266
Cell4		0.174		0.148
Cell5		0.100		0.083
Cell6		0.072		0.047
Cell7		0.041		0.027
Cell8		0.016		0.015
Reactor 2				
Experiment	pH	[NH2Cl] mg/l	Nt/No (observed)	Nt/No (predicted)
Run 1	7.01	1.2	0.029	0.032
Run 2	7.00	2.1	0.006	0.002

Equation 6 was also used to predict survival ratios for reactor 2 (N=59). As shown in Table 3 the predicted and observed ratios corresponded well for this reactor too. When the predicted survival ratios are compared to the measured ratios, a good correlation (R^2 = 0,94) is observed as shown in Fig. 7.

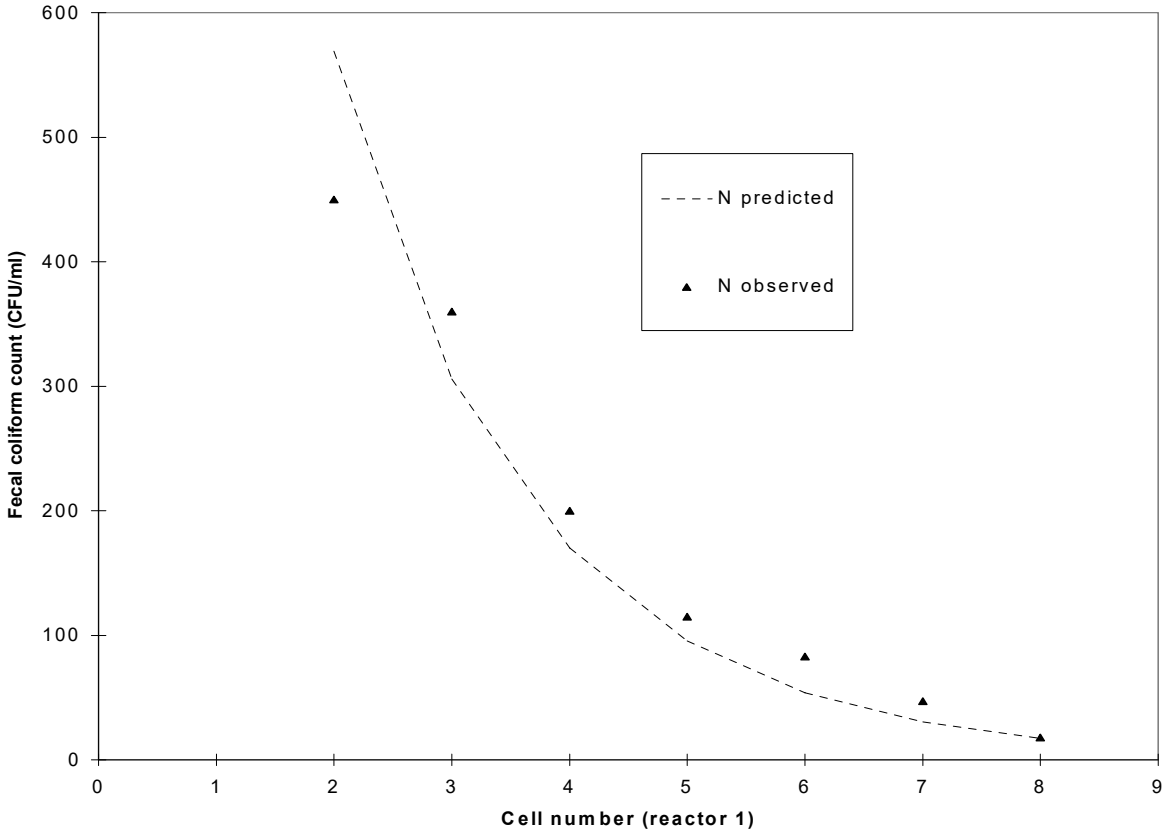


Figure 7: Evaluation of the predictive capability of Eq. (6)

Conclusions

- This study shows that the disinfectant capability of monochloramine is not significantly affected by chlorine demand-causing materials as is the case with free chlorine.
- The effect of pH on the disinfectant capability of monochloramine as measured in this study was not as significant as measured by Ward et al. (1984).
- Of the three models evaluated for accuracy in the batch inactivation experiments, the series-event kinetic model (Eq. (6)) gave the best fit to the measured data.

- The fitted parameter of the series-event model, K, displayed a more consistent variation with monochloramine and pH concentration while the reaction coefficients of the other models vary in a more random fashion. This makes the series-event model the most suitable inactivation model for the water tested.
- The series-event model combined with the tanks-in-series model gives accurate predictions of the survival ratios measured in the continuous-flow systems.
- The series-event model in combination with a tracer study provides an accurate method to predict the performance of a continuous-flow CCT from batch inactivation studies using monochloramine as disinfectant.
- This study shows that the behaviour of a continuous-flow CCT can be accurately predicted from batch experiments conducted in the laboratory. This provides a method that employs data from simple batch experiments conducted in the laboratory for the design of continuous-flow monochloramine disinfection systems.

Acknowledgement

The research presented in this paper was made possible by the financial assistance of the Water Research Commission. Mr Nico Oosthuizen is thanked for his assistance with the tracer experiments.

References

AIETA EM, BERG JD, ROBERTS PV and COOPER RC (1980) Comparison of chlorine dioxide in wastewater disinfection. *J. Water Pollut. Control Fed.* **52**(4) 810-822.

AMERICAN SOCIETY OF CIVIL ENGINEERS (ASCE) (1986) Chloramines a better way?. *Civ. Eng.* **56**(4) 50-51.

BERMAN D, SULLIVAN R and HURST CJ (1992) Effect of the method of preparing monochloramine upon the inactivation of MS2 coliphage, *Escherichia coli* and *Klebsiella pneumoniae. Can. J. Microbiol.* **38**(1) 28-33.

CARNIMEO D, CONTINI E, DI MARINO R, DONADIO F, LIBERTI L and RANIERI E (1994) Wastewater disinfection by UV at Trani municipal plant. *Water Sci. Technol.* **30**(4) 125-132.

CHICK HE (1908) An investigation of the laws of disinfection. *J. Hyg.* **8** 92-158.

DICE JC (1985) Denver's seven decades of experience with chloramination. *J. Am. Water Works Assoc.* **77**(1) 34-37.

HAAS CN, JOFFE J, HEATH M, JACANGELO J and ANMANGANDLA U (1998) Predicting disinfection performance in continuous flow systems from batch inactivation studies. *Proceedings of the Nineteenth Biennial Conference of the International Association on Water Quality, Vancouver, Canada, June 21 - 26.*

HOM LW (1972) Kinetics of chlorine disinfection of an ecosystem. *Journal of the Sanitary Engineering Division ASCE* **98** (SA1) 183-194.

JACANGELO JG, PATANIA NL, REAGAN KM, AIETA EM, KRASNER SW and McGUIRE MJ (1989) Ozonation: Assessing its role in the formation and control of disinfection by-products. *J. Am. Water Works Assoc.* August.

JOHNSON JD and JENSEN JN (1986) THM and TOX formation: Routes, rates and precursors. *J. Am. Water Works Assoc.* **78**(4) 156-162.

KOUAME Y and HAAS CN (1991) Inactivation of *E. coli* by combined action of free chlorine and monochloramine. *Water Res.* **25**(9) 1027-1032.

KREFT P, UMPHRES M, HAND JM, TATE C, McGUIRE MJ and TRUSSEL RR (1985) Converting from chlorine to chloramines: A case study. *J. Am. Water Works Assoc.* **77**(1) 38-45.

LEVENSPIEL O (1972) *Chemical Reaction Engineering*. John Wiley & Sons, New York.

PALIN AT (1974) Chemistry of modern water chlorination. *Water Services* **78** (935).

REYNOLDS G, MEKRAS C, PERRY R and GRAHAM N (1989) Alternative disinfectant chemicals for trihalomethane control - A review. *Environ. Technol. Letters* **10** 591- 600.

RICE EW, COVERT TC, WILD DK and BERMAN D (1993) Comparative resistance of *Escherichia coli* and enterococci to chlorination. *J. Environ. Sci. and Health* **A28**(1) 89-97.

SEVERIN BF, SUIDAN MT and ENGELBRECHT RS (1984) Series-event kinetic model for chemical disinfection. *J. Environ. Eng.* **110**(2) 430-439.

SHULL KE (1981) Experience with chloramines as primary disinfectants. *J. Am. Water Works Assoc.* **73**(2) 101-104.

SMITH JM (1981) *Chemical Engineering Kinetics*. McGraw-Hill, New York.

Standard Methods for The Examination of Water and Waste Water. 17th Ed. APHA (1989)

TEEFY SM and SINGER PC (1990) Performance and analysis of tracer tests to determine compliance of a disinfection scheme with the SWTR. *J. Am. Water Works Assoc.* **82**(12) 88-98.

WARD NR, WOLFE RL AND OLSON B (1984) Effect of pH, application technique, and chlorine-to-nitrogen ration on disinfectant activity of inorganic chloramines with pure culture bacteria. *Appl.Environ. Microbiol.* **48**(3) 508-514.

WATSON HE (1908) A note on the variation of the rate of disinfection with change in the concentration of the disinfectant. *J. Hyg.* **8** 536-592.

WHITE GC (1992), *Handbook of Chlorination and Alternative Disinfectants,* New York: Van Nostrand.

YAMAMOTO K, FUKUSHIMA M and ODA K (1988) Disappearance rates of chloramines in river water. *Water Res.* **22**(1) 79-84.

Appendix: Design Example

The following example is included to show how the method discussed above can be applied to a situation where a chloramination system is to be retrofitted to an existing CCT. The following data are available

Table A1: Available data

Parameter	Units	Value
Volume of CCT (V)	m^3	450
Flow rate (F)	m^3/min	30
Theoretical Hydraulic retention time (T)	min	15
Design pH	pH	7,0
Desired effluent fecal coliform count	CFU/100 ml	<1
Initial fecal coliform count	CFU/100 ml	100 000

The objective is to determine the monochloramine concentration required to obtained a desired inactivation of fecal coliform bacteria.

Step 1:

Conduct a tracer study on the CCT's and analyse the data with the tanks-in-series model. The following table contains typical data obtained from a tracer experiment where 400g of lithium was injected as a pulse input into the CCT described in table A1:

Table A2: Data obtained from tracer study.

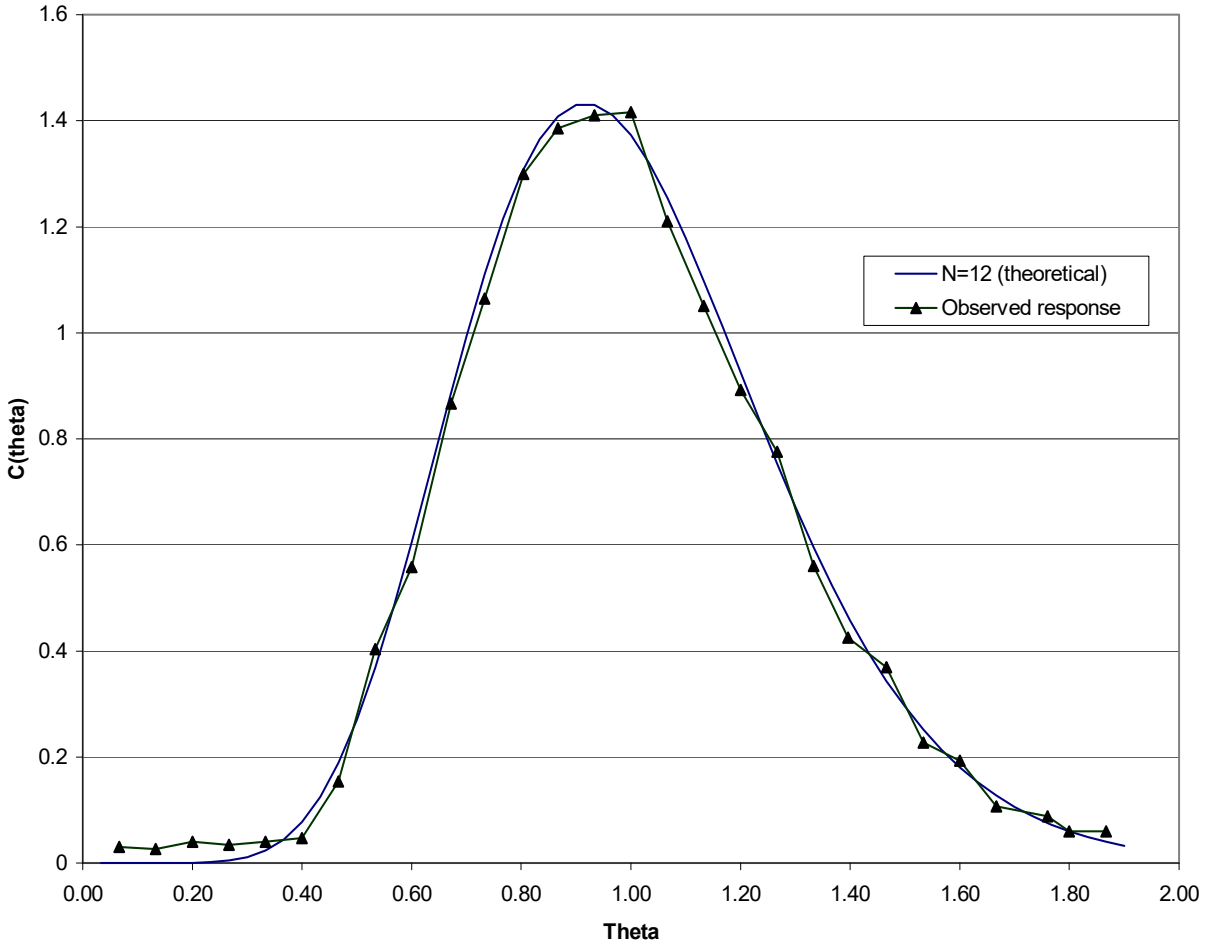
Time (min)	Lithium concentration (mg/l)	θ	Cθ	Recovery of lithium (g)
1	0.03	0.07	0.03	0.80
2	0.02	0.13	0.03	0.69
3	0.04	0.20	0.04	1.07
4	0.03	0.27	0.03	0.91
5	0.04	0.33	0.04	1.07
6	0.04	0.40	0.05	1.25
7	0.14	0.47	0.15	4.11
8	0.36	0.53	0.40	10.75
9	0.50	0.60	0.56	14.88
10	0.77	0.67	0.87	23.10
11	0.95	0.73	1.06	28.37
12	1.16	0.80	1.30	34.65
13	1.23	0.87	1.39	36.96
14	1.25	0.93	1.41	37.60
15	1.26	1.00	1.43	37.76
16	1.08	1.07	1.21	32.27
17	0.93	1.13	1.05	28.03
18	0.79	1.20	0.89	23.79
19	0.69	1.27	0.78	20.69
20	0.50	1.33	0.56	14.93
21	0.38	1.40	0.43	11.33
22	0.33	1.47	0.37	9.84
23	0.20	1.53	0.23	6.05
24	0.17	1.60	0.19	5.15
25	0.10	1.67	0.11	2.85
26	0.08	1.76	0.09	2.34
27	0.05	1.80	0.06	1.59
28	0.05	1.87	0.06	1.60
				Total mass 394.4

To obtain the tracer response curve, Cθ is plotted vs. θ. Where Cθ and θ are normalised concentration and time values respectively. These values are calculated as follows:

$$C\theta = \frac{\text{Concentration (C)}}{\text{Dose Concentration } (C_o)} \quad \text{and} \quad \text{Dose concentration } (C_o) = \frac{\text{Mass of tracer injected}}{\text{Reactor volume (V)}}$$

$$\theta = \frac{\text{Time (t)}}{\text{Theoretical hydraulic retention time (T)}}$$

The tracer response data are represented on the curve below:



The recovery for each time interval is calculated as the product of the measured tracer concentration in the interval, the time elapsed in the interval and the flow. (Mass = $C \times \Delta t \times F$). The total recovery is then determined by obtaining the sum of recoveries over all the time intervals:

$$\text{Tracer recovered} = \frac{\text{Sum of recoveries}}{\text{Mass of tracer injected}} = \frac{394{,}4\text{g}}{400\text{g}} = 98{,}6\% \ .$$

To obtain the number of theoretical CSTRs equivalent to the CCT, the maximum value of $C\theta$, ($C\theta_{max}$), is used together with the following equation and solving for N:

$$C_{\theta_{\max}} = \frac{N(N-1)^{N-1}}{(N-1)!} e^{-(N-1)}$$

From Table A2 $C\theta_{max}$ is equal to 1,43 which corresponds to N=12.

Step 2:

Determine the required survival ratio (N_e/N_i):

$$\frac{N_e}{N_i} = \frac{\text{Count required in effluent}}{\text{Initial count}} = \frac{1}{100\,000} = \frac{N_t}{N_0}$$

Step 3:

Use Eq. (B-1) (Appendix B) to determine the apparent kinetic constant, K, required to obtain the desired inactivation (survival ratio):

$$\frac{N_t}{N_o} = \left(\frac{1}{1+K\tau'}\right)^N \cdot \sum_{i=0}^{j-1} \left[\frac{i+N-1}{N-1}\right]\left(\frac{K\tau'}{1+K\tau'}\right)^i$$

(B-1)

Use the best fit value of j=2 as obtained in the experimental work above (this may vary from one effluent to another). The value of τ' is obtained by dividing the theoretical retention time of the CCT by the N value obtained in **Step 1** (N=12). Thus τ' = 1.25 min.

Substitute the values of τ' (1,25 min), N (12) and the survival ratio, N_t/N_o (0,0001), and calculate the corresponding value of K. The K value obtained in this way is 1.34 min^{-1}.

Step 4:

Use the K value obtained in Step 3 (1,34 min^{-1}) and evaluate the monochloramine concentration required at the relevant pH (pH7) from Fig. 3. At this K value and pH, a monochloramine concentration of 4,2 mg/l is required to effect the desired inactivation of fecal coliforms.