

**DISINFECTION OF PURIFIED SEWAGE EFFLUENT
WITH MONOCHLORAMINE**

by

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ABSTRACT

The disinfection of purified wastewater is affected by various different factors that are complex in their nature and variability. Numerous laboratory investigations have been conducted to quantify these factors by studying them in isolation. The laboratory investigations often make use of distilled water, pure bacterial cultures and bench scale batch testing which does not reflect the complex chemistry nor the hydraulic behaviour of a full-scale disinfection contact chamber. This presents some difficulty to the designer of a disinfection facility, who must extrapolate these findings to the operational conditions present in a full-scale wastewater treatment plant. The design of a full-scale disinfection process would therefore 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.

This dissertation discusses:

- The fundamental chemistry relevant to disinfection systems where chlorine and nitrogen compounds are present.
- The factors affecting the kinetics of disinfection processes and mathematical formulation thereof.

- Hydraulic considerations relevant to disinfection and methods for incorporating the hydraulic behaviour of a contact chamber into the equations used to predict the behaviour of continuous flow disinfection systems.

The principal mathematical models of disinfection found in the literature, were experimentally evaluated in batch disinfection studies conducted on the effluent of a full-scale wastewater treatment plant. The most accurate model was verified for use in the modelling of continuous flow disinfection of the same effluent.

Conclusions are:

- The disinfectant capability of monochloramine is not significantly affected by chlorine demand-causing material as is the case with free chlorine and was found to be adequate in achieving the required disinfection standards.
- The series-event kinetic model was found to be the most suitable inactivation model and combined with the tanks-in-series model gives accurate predictions of the survival ratios measured in the continuous-flow systems.
- This study shows that the behaviour of a continuous-flow chlorine contact chamber (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.

Keywords: Disinfection, Wastewater, Monochloramine, Chloramines, Contact Chambers, Disinfection Kinetics, Reactor Design.

SAMEVATTING

Die ontsmetting van gesuiwerde afvalwater word deur 'n verskeidenheid komplekse en veranderlike faktore beïnvloed. Verskeie laboratorium ondersoekes is al onderneem om hierdie faktore te kwantifiseer deur elkeen in isolasie te bestudeer. Studies van hierdie aard maak dikwels gebruik van gedistilleerde water, rein-kultuur bakterieë en laboratorium skaal beker toetse wat nie die komplekse chemiese en hidrouliese gedrag van 'n volskaalse ontsmettings reaktor weerspieël nie. Dit bemoeilik die taak van die ontwerper wat hierdie data moet ekstrapoleer na die bedryfs toestande van 'n volskaalse afvalwater behandelingsproses. Die ontwerp van 'n volskaalse proses sal dus verbeter kan word indien die resultate van beker toetse wat op riool uitvloeiels in die laboratorium uitgevoer is, gekoppel kan word aan die hidrouliese gedrag van 'n kontinue-vloei kontak kamer.

Hierdie verhandeling bespreek:

- Die fundamentele chemie betrokke by ontsmettingstelsels waar chloor- en stikstof verbindings teenwoordig is.
- Die faktore wat die kinetika van ontsmettings-prosesse beïnvloed en die wiskundige formulering daarvan.
- Hidrouliese oorwegings betrokke by ontsmetting en die metodes wat gebruik kan word om die hidrouliese gedrag van 'n chloor kontak kamer in ag te neem tydens wiskundige voorspellings van die werking van 'n kontinue-vloei ontsmettingstelsel.

Gepubliseerde wiskundige modelle, is eksperimenteel ge-evalueer deur middel van ontsmettings toetse wat op die uitvloeisel van 'n volskaalse afvalwater behandelings aanleg uitgevoer is. Die mees akkurate model is bevestig deur dit toe te pas op die ontsmetting van dieselfde uitvloeisel in 'n kontinue vloei stelsel.

Die volgende gevolgtrekkings word gemaak:

- Die ontsmettings-vermoë van monochloor-amien word nie merkbaar beïnvloed deur die teenwoordigheid van verbindings wat 'n chloor aanvraag veroorsaak nie.
- Monochloor-amien is 'n voldoende ontsmettingsmiddel vir die vereiste ontsmettings standaard.
- Die "reeks-gebeurtenis"-model in kombinasie met die "reaktore-in-serie"-model het die mees akkurate voorspellings van die waargenome oorlewings verhoudings gelewer.
- Hierdie studie demonstreer hoe die gedrag van 'n kontinue vloei chloor kontak kamer voorspel kan word deur gebruik te maak van data afkomstig van beker toetse wat in die laboratorium uitgevoer is. Dié metode gebruik eenvoudige laboratorium toetse vir die ontwerp van kontinue vloei ontsmettingstelsels met monochloor-amien as ontsmettingsmiddel.

Sleutelwoorde: Ontsmetting, Afvalwater, Monochloor-amien, Chloor-amien, Kontak Kamer, Ontsmettings Kinetika, Reaktor Ontwerp.

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1 INTRODUCTION

The South African General and Special Standards stipulate that treated sewage effluent should comply with a standard of nil faecal 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. 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 ($\text{HOCl} + \text{OCl}^-$). This is also the practice in South Africa as was confirmed by a recent survey reported in Appendix A (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).

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). 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 of the reactor used (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 efficiency of monochloramine under operational conditions typically found at a South African wastewater treatment

plant, and to show how this information may be used in the design calculations of a chloramine disinfection system.

2 THE CHEMISTRY OF WASTEWATER CHLORINATION

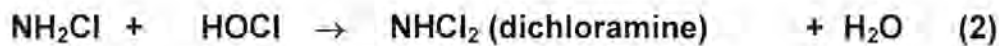
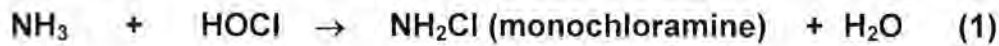
Wastewater is a complex mixture of chemical and microbiological entities (Ekama *et al.* 1984). The chemical nature of wastewater in particular is of great significance to the disinfection process. The reason for this is that any chemical species present in the wastewater may potentially react with the disinfectant resulting in compounds with lowered disinfection efficiencies as reported by Ward *et al.*, (1984). Research by White *et al.*, (1983) has shown that nitrogen compounds play a central role in the disinfection of wastewater.

2.1 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 $\text{NH}_n\text{R}_{3-n}$ (e.g. NH_3 and amino acids), 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).

2.2 The Breakpoint Curve

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



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 ($\text{Cl}_2:\text{NH}_3\text{-N}$)
- initial free chlorine and ammonia concentrations

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

Palin (1974) showed that the dominant species formed in the overall reaction is

dependent on the chlorine to nitrogen mass ratio ($\text{Cl}_2:\text{N}$). 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.

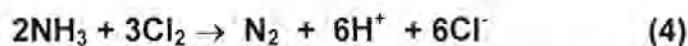
Table 1 illustrates the effect of pH and the $\text{Cl}_2:\text{NH}_3\text{-N}$ mass ratio on the rates of formation of the different chloramine species. The table shows how a higher degree of hydrogen substitution is favoured by low pH values, high $\text{Cl}_2:\text{NH}_3\text{-N}$ mass ratios and 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 1: Summary of the conditions required for the formation of the different chloramine species (White, 1992)

Parameter	Monochloramine	Dichloramine	Trichloramine
Optimal pH	8,3	5 - 7	<5
$\text{Cl}_2:\text{NH}_3\text{-N}$ (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 great importance of the reactions in Equations 1 to 3 to the practice wastewater chlorination was demonstrated by Griffin and Chamberlin (1941). 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 Equation 1 up to a $\text{Cl}_2:\text{NH}_3\text{-N}$ mass ratio of 5:1 (which is equivalent to a 1mol of Cl_2 : 1mol of $\text{NH}_3\text{-N}$). The concentration of total chlorine residuals does not however continue to increase with further addition of chlorine but actually decreases up to a $\text{Cl}_2:\text{NH}_3\text{-N}$ 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 1). This behaviour is explained by the following equation presenting the overall *breakpoint reaction*:



This reaction explains the disappearance of combined chlorine residuals 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.

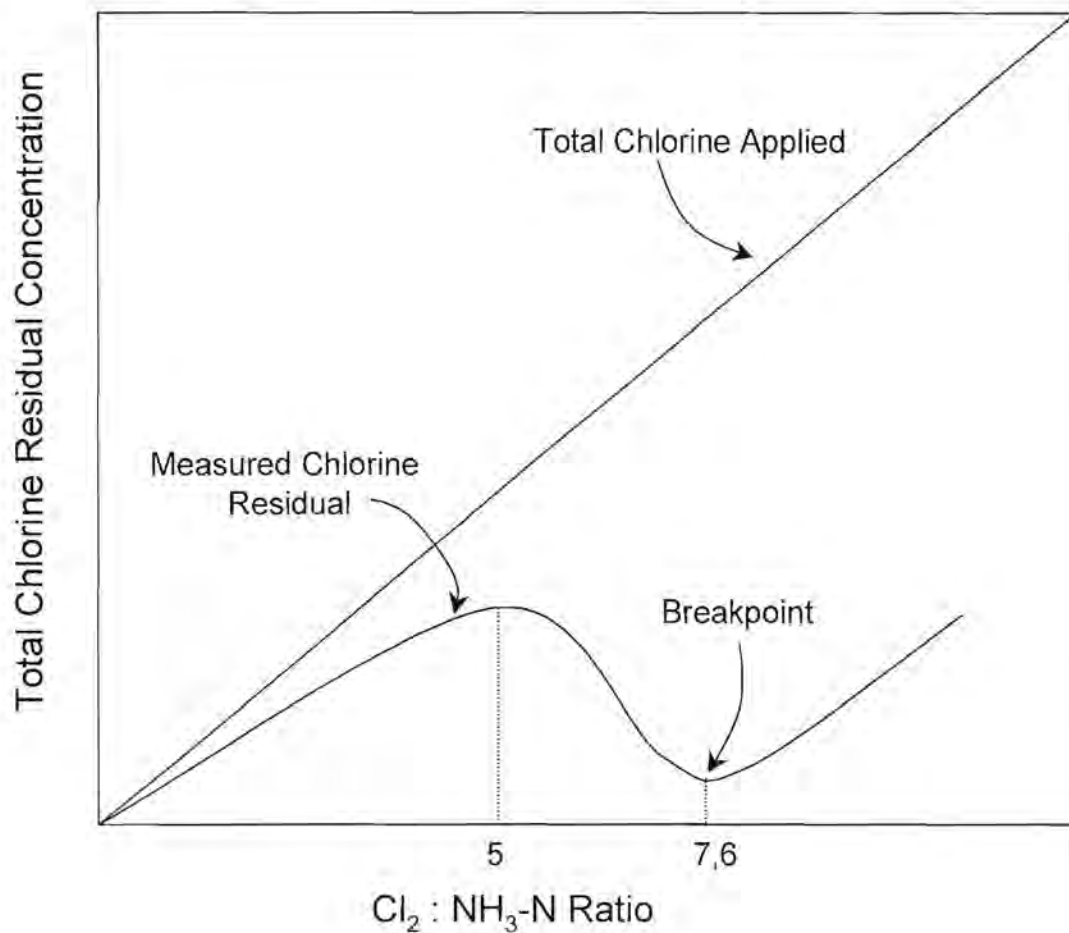


Figure 1: The breakpoint curve

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 a rate of 7,6 mg of Cl_2 /mg of $\text{NH}_3\text{-N}$ 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 is designed to rely upon free chlorine alone 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. Variations in the water chemistry of a specific plant will also result in variations in disinfection efficiency at the plant.

2.3 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.* (1984), the Total Kjeldahl Nitrogen (TKN) of the influent to South African municipal wastewater treatment plants can be divided into the following:

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

Each of these fractions behaves differently as the wastewater flows through the different treatment processes employed at a specific treatment plant. Whether the treatment plant practices full or partial nitrification is of particular importance to the composition of nitrogenous compounds present in the effluent.

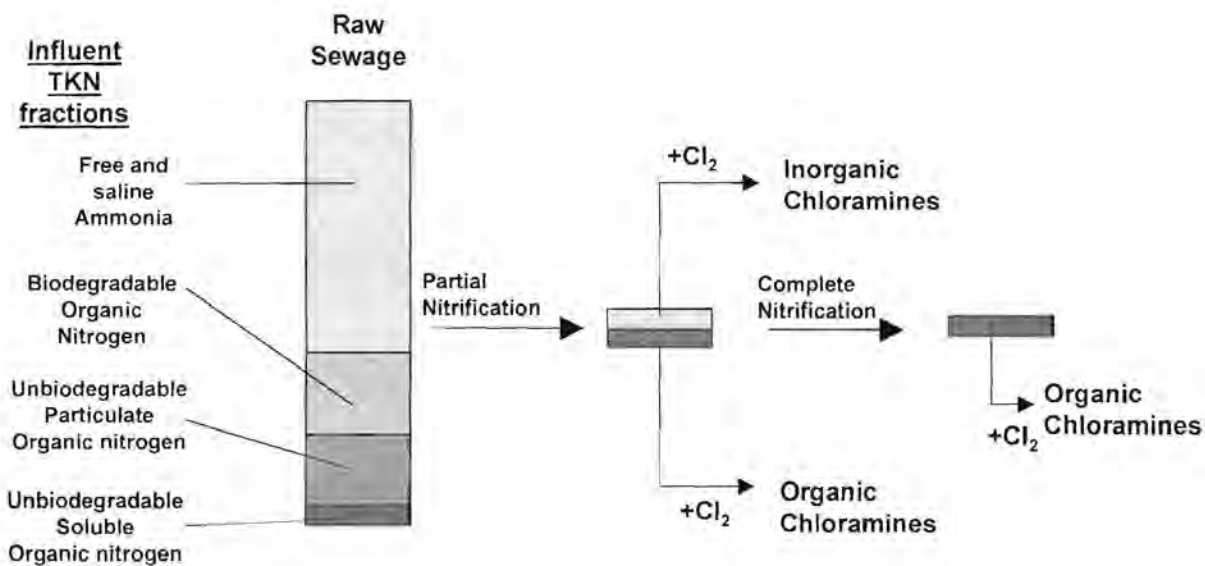


Figure 2: The effect of the degree of nitrification on tkn fractionation in the effluent of a wastewater treatment plant.

Figure 2 shows how the different fractions of the influent TKN change during treatment of the wastewater. Biodegradable organic nitrogen is rapidly converted by heterotrophic organisms to free and saline ammonia, while the unbiodegradable particulate nitrogen is removed along with the activated sludge, from the waste stream by secondary settling and filtration. 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 and Beebe. (1983), who conducted an investigation on a number of US treatment plants that experienced difficulty in disinfecting nitrified effluents. 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 and Baker, 1983).

2.4 Other Organic Compounds

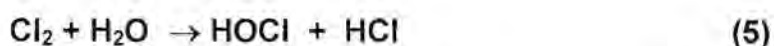
The reaction between chlorine and organic compounds have become the source of some debate since the early seventies when it was discovered that certain disinfection

by-products (DBP's) were formed during the chlorination of drinking water. 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. A benefit of using chloramines is a reduction in the formation of THM's as reported by Reynolds, *et al.*, (1989). 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.

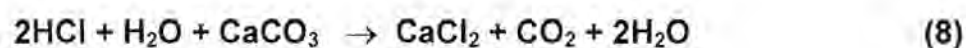
2.5 Inorganic compounds

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 has 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 and Beebe, 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 and Chamberlin, 1941):



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



This reaction shows that chlorination of water can cause a drop in pH if sufficient alkalinity is not available to buffer the reaction. Table 2 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 2: Some examples of the reactions of chlorine consuming inorganic species.

Species	Reaction	Cl ₂ demand (mg Cl ₂)
NO ₂ ⁻	HOCl + NO ₂ ⁻ → NO ₃ ⁻ + HCl	5,06/mgNO ₂ ⁻ -N
Fe ²⁺	2Fe ²⁺ + Cl ₂ → 2Fe ³⁺ + 2Cl ⁻	0,64/mgFe ²⁺
Mn ²⁺	Mn ²⁺ + Cl ₂ + 2H ₂ O → MnO ₂ + 4H ⁺ + 2Cl ⁻	1,29/mgMn ²⁺
H ₂ S	H ₂ S + 4Cl ₂ + 4H ₂ O → H ₂ SO ₄ + 8HCl	8,34/mgH ₂ S
CN ⁻	5Cl ₂ + 10OH ⁻ + 2CN ⁻ → 2HCO ₃ ⁻ + 10Cl ⁻ + N ₂ + 4H ₂ O	6,82/mgCN ⁻
C	C + 2Cl ₂ + 2H ₂ O → 4HCl + CO ₂	11,82/mgC
Alkalinity	Cl ₂ + (Chlorine demand) + CaCO ₃ → CaCl ₂ + CO ₂ + (oxidised compounds)	1,4mg Alkalinity as CaCO ₃ /mgCl ₂ consumed

2.6 The Significance Of Chlorine Chemistry On Wastewater Disinfection

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

- Although chlorine is a very effective disinfectant it is also very reactive to a host of substances present in wastewater resulting in wasteful side reactions that do not contribute to disinfection.
- Conventional disinfection with chlorine requires excessively high chlorine dosages where complete nitrification is practised.
- Chloramines have been shown to have disinfective capability and forms rapidly when chlorine is applied to wastewater containing ammonia.
- 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 KINETICS OF WASTEWATER DISINFECTION

The disinfection of wastewater with chloramines is influenced by five major factors, i.e. the number and type of the target organisms, disinfectant concentration, contact time, temperature and water quality.

3.1 Number And Type Of Target Organisms

3.1.1 The Indicator Organism

The microbiological composition of raw 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 each individual pathogenic species. It is for this reason that testing methods, which 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.

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

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

3.1.2 The Number Of Organisms Present

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.

3.2 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 chlorine 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 strengths 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.

3.3 Contact Time

Another critical factor affecting the disinfection process is the contact time, as it is a characteristic inherent to the disinfection contact chamber employed. 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 (1908) 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 Equation 10, Table 3).

3.4 Temperature And Water Quality

The effect of temperature on disinfection kinetics is to increase the rate of inactivation with increasing temperature. This means that a given percentage inactivation will be achieved in a shorter period of time at a higher temperature as shown by the following form of the van't Hoff-Arrhenius relationship from Tchobanoglous and Burton (1991: 330):

$$\ln \frac{t_1}{t_2} = \frac{E(T_2 - T_1)}{RT_1T_2} \quad (9)$$

Where: t_1 and t_2 = time for a given percentage inactivation at temperatures T_1 and T_2

E = activation energy, J/mol

R = gas constant, 8,314J/mol.K

The chemical quality of the effluent to be disinfected will affect the demand that the effluent has for the disinfectant used. This fact was extensively shown for completely nitrified effluents (Section 2) that have a large demand for free chlorine but little or no demand for the chloramine compounds. Various chemical reactions 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 thus show better

disinfection results for one disinfectant that may show poor capabilities compared to another when tested in demand free water in the laboratory. This once again emphasises the importance of evaluating a disinfectant under the actual operating conditions found in practise.

3.5 Kinetic Models For 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 3.

The earlier models developed by Chick (1908) and Watson (1908) was based on the principles of first order kinetics and is represented as Equation 10. 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 Equation 11 and 12.

Equation 13 is known as the series-event kinetic model and was proposed by Severin *et al.*, in 1984. The 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 Eqn. 13) and the organism is inactivated. This theory proposes that a certain number of interactions, between the individual organism and the disinfectant molecule, are required for inactivation.

As discussed above, free chlorine is a reactive chemical that will decay when it comes into contact with wastewater. The resulting decrease in disinfectant concentration over time affects the rate of inactivation and is taken into account by Eqn. 14, presented by Haas *et al.* (1998).

The equations given in Table 3 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 3 must 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.

4 CONTINUOUS FLOW SYSTEMS

Before it becomes possible to extrapolate the findings of batch disinfection studies conducted in a laboratory beaker to disinfection in the full-scale contact tanks typically employed at wastewater treatment plants, it is necessary to understand and quantify the hydraulic behaviour and to modify the batch kinetic models accordingly.

Table 3: Summary of the principle inactivation models.

Model	Eq n.	Author	Comments
$\ln \frac{N_t}{N_o} = -kC^n t$	10	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.
$\ln \frac{N_t}{N_o} = -kC^n t^m$	11	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).
$\ln \frac{N_t}{N_o} = -k' t^m$	12	Hom (1972)	Modification of Eqn. (2) for constant disinfectant concentration. $k' = kC^n$ in Eqn. (2).



Model	Eq n.	Author	Comments
$\frac{N_t}{N_o} = e^{-kct} \sum_{i=0}^{j-1} \frac{(kct)^i}{i!}$	13	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
$\ln \frac{N_t}{N_o} = -\left(\frac{m}{nk^*}\right)^m k(C_o)^n \left[1 - \exp\left(-\frac{nk^*t}{m}\right)\right]^m$	14	Haas <i>et al.</i> (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.
<p>N_o = initial concentration of organisms residual decay rate</p> <p>N_t = organism concentration at time t</p> <p>C = disinfectant concentration</p> <p>k = reaction rate constant</p> <p>m = empirical constant</p> <p>n = coefficient of dilution</p> <p>k^* = first-order</p> <p>j = lethal number of reactions</p>			

4.1 Hydraulic Behaviour Of Continuous Flow Systems

Not all the elements of a fluid pass through a continuous flow system (reactor) along the same flow path as some short-circuiting may take place. This creates a distribution in the residence time of the different fluid elements as shown by Levenspiel (1972: 255). The distribution is called the residence time distribution (RTD). Chemical 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 be 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 $N = \infty$ (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.

4.2 Predicting The Behaviour Of A Continuous Flow System From Batch Kinetic Data

The tanks-in-series model was 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_0) 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:

$$\frac{N_t}{N_0} = \left(\frac{1}{1 + K\tau'} \right)^N \cdot \sum_{i=0}^{j-1} \left[\frac{i + N - 1}{N - 1} \right] \left(\frac{K\tau'}{1 + K\tau'} \right)^i \quad (15)$$

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

τ' = residence time in one CSTR

N = number of equally sized CSTRs in series

N_0 = initial concentration of organism

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

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

5 EXPERIMENTAL INVESTIGATION INTO THE EFFICIENCY OF WASTEWATER DISINFECTION WITH MONOCHLORAMINE

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 faecal coliforms in the effluent of a typical wastewater treatment plant.
- 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 (Eqn. (15)) and used 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 Eqn. (15) to verify the use of this model under operational conditions.

5.1 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.

5.2 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 ammonium chloride (NH_4Cl) solution (Merck) to produce 500ml of a NH_2Cl concentration of ca. 2g/l ($\text{Cl}_2:\text{N}$ 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).

5.3 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 $25^\circ\text{C}\pm 1^\circ\text{C}$ 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 faecal coliform count (N_0). 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 thiosulphate solution of sufficient strength to neutralise the monochloramine residual as reported by Ward *et. al.* (1984). After dilution the surviving faecal coliform bacteria were counted taking into account the dilution of the neutralising thiosulphate solution.

5.4 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 3 and 4 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 faecal coliform numbers. The operating conditions and results of this experiment are shown in Table 5.

5.5 Enumeration Of Bacteria

The test organism used was the faecal 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 faecal 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.

5.6 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).

5.7 Data Analysis

Because the more recent models (Eqs. (13) and (14)) are more complex than the older ones (Eqs. (10) (11) and (12)), 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. To find the most accurate model for batch inactivation kinetics, the data obtained from the batch inactivation studies were fitted to Eqs. (10), (12), (13) and (14) (Eqn. (10) showed significant deviation from the observed data and no further attempt was made to use this equation). Equation (12) was linearized and fitted with Microsoft Excel 97 software (Microsoft corporation, California, 1993) using linear regression. Equation (13) 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 Eqn. (13). The least square best fit

value of K was then recorded (Severin, *et al.*, 1984). Equation (14) 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 (Eqn. 15) was used (Severin *et al.*, 1984)
- The value of K was graphically evaluated from Figure 5 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 4.

The N value for each reactor, as obtained from the tracer experiment, was used in Eqn. (15).

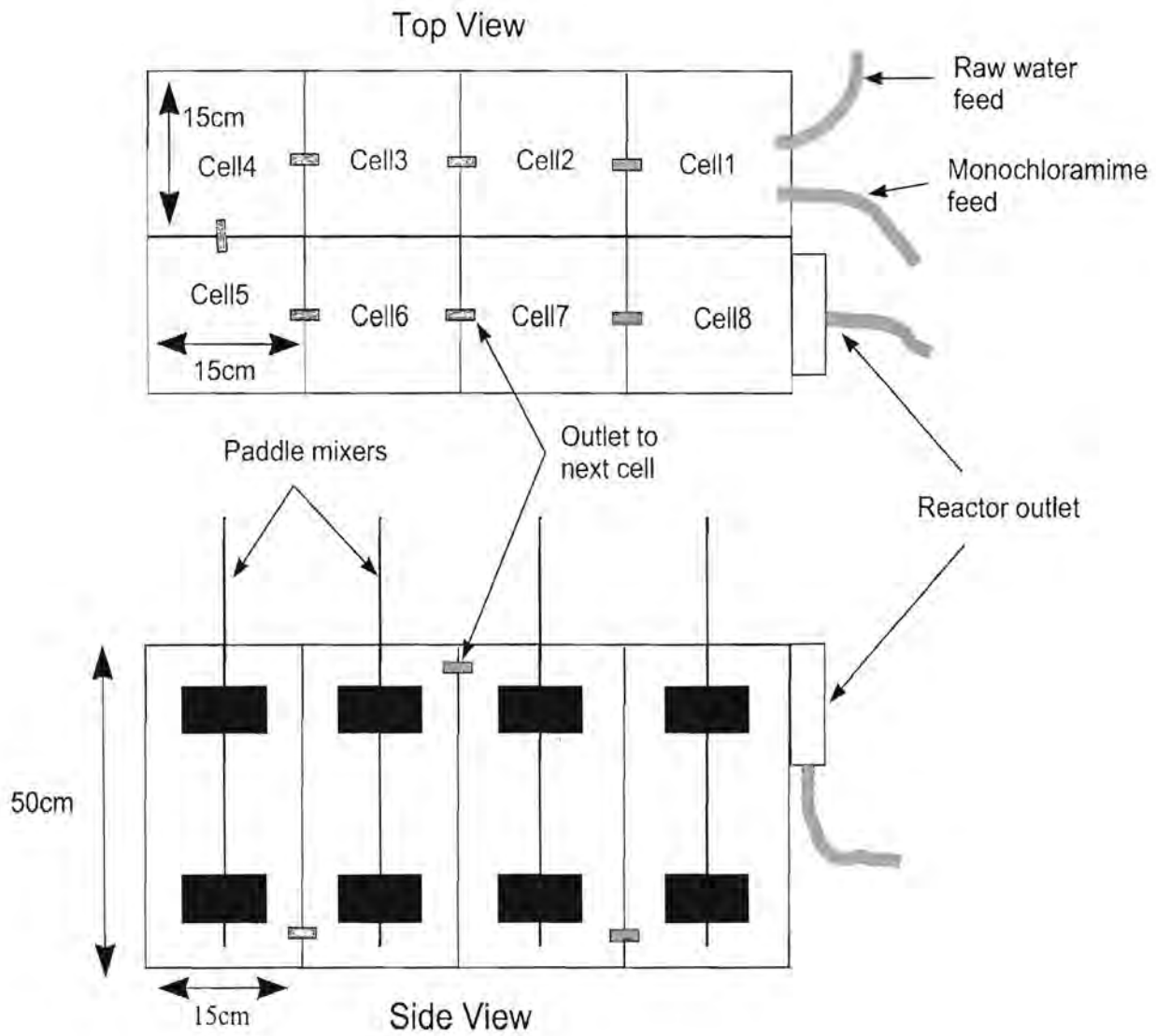


Figure 3: CSTRs in series (Reactor 1)

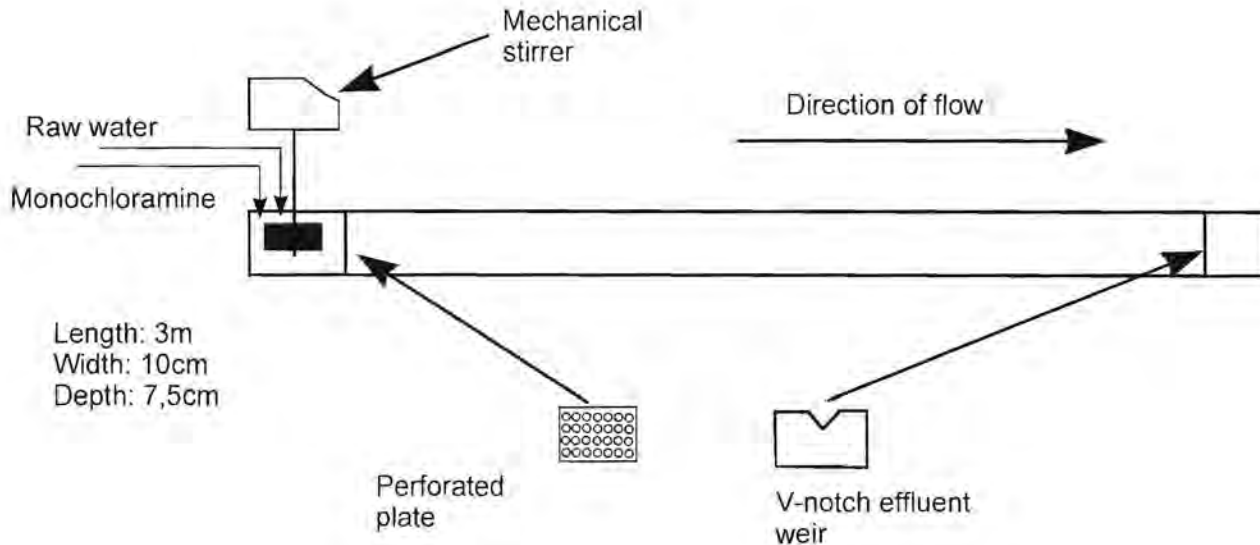


Figure 4: Channel (Reactor 2)

6 RESULTS AND DISCUSSION

6.1 Batch Inactivation Studies

The fitted parameters and correlation coefficients (R^2) for each of the models evaluated are given in Table 4. Referring to Table 4, there are 5, 11 and 8 sets of data that can be fitted to Eqs. (12), (13) and (14) respectively with a correlation coefficient greater than 0,95. Equation (13) 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 (Eqn. (15)) and monochloramine concentration is shown in Fig.

5.

Table 4: Comparison of the correlation of different kinetic models for batch inactivation studies.

Exp No.	[NH ₂ Cl] 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.

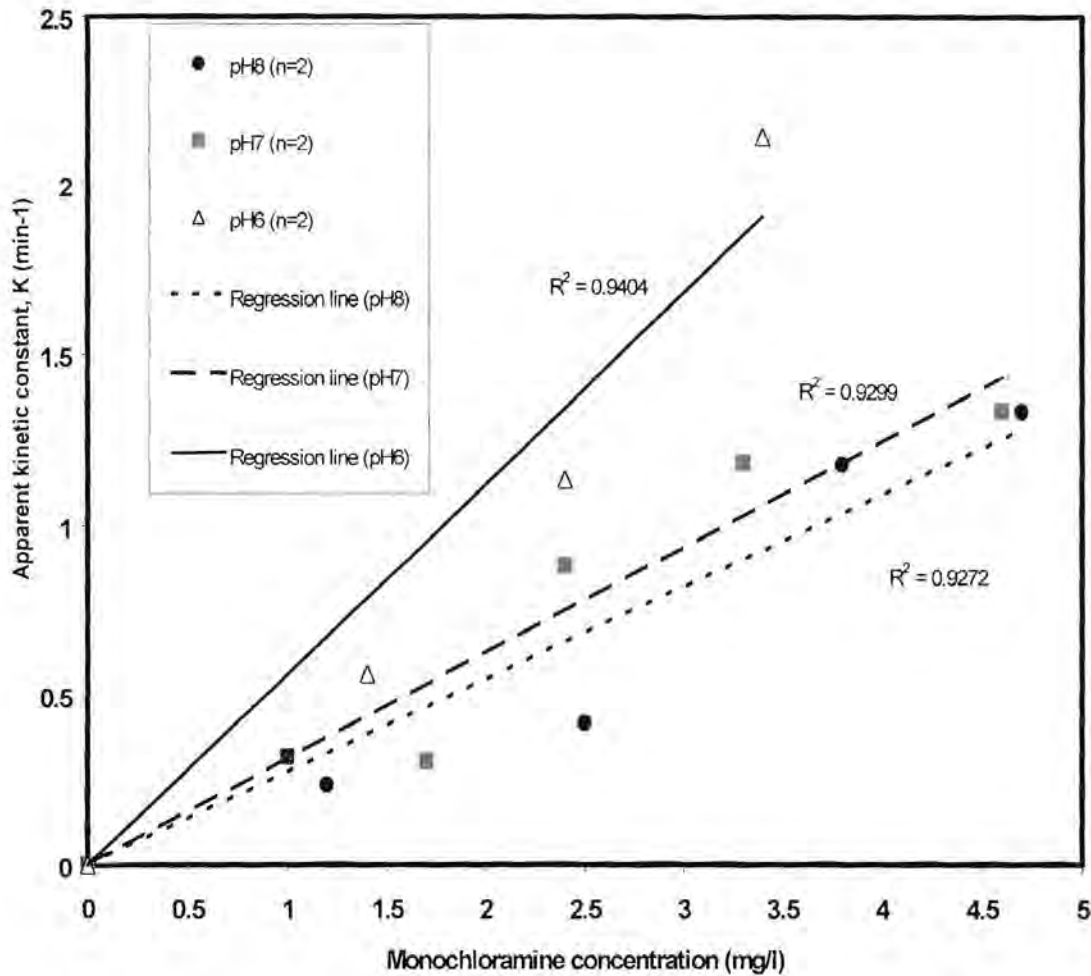


Figure 5: The relationship between the apparent kinetic constant (K) and monochloramine concentration as measured at different pH values in batch experiments.

The relationship between monochloramine concentration and the time required to effect a 99% reduction in faecal coliform numbers (t_{99}) at three different pH values is shown in Fig. 6. The graph was generated using Eqn. (3) to determine the t_{99} values. The data are presented in this way (i.e. using Eqn (3) instead of Eqn (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. 6) 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).

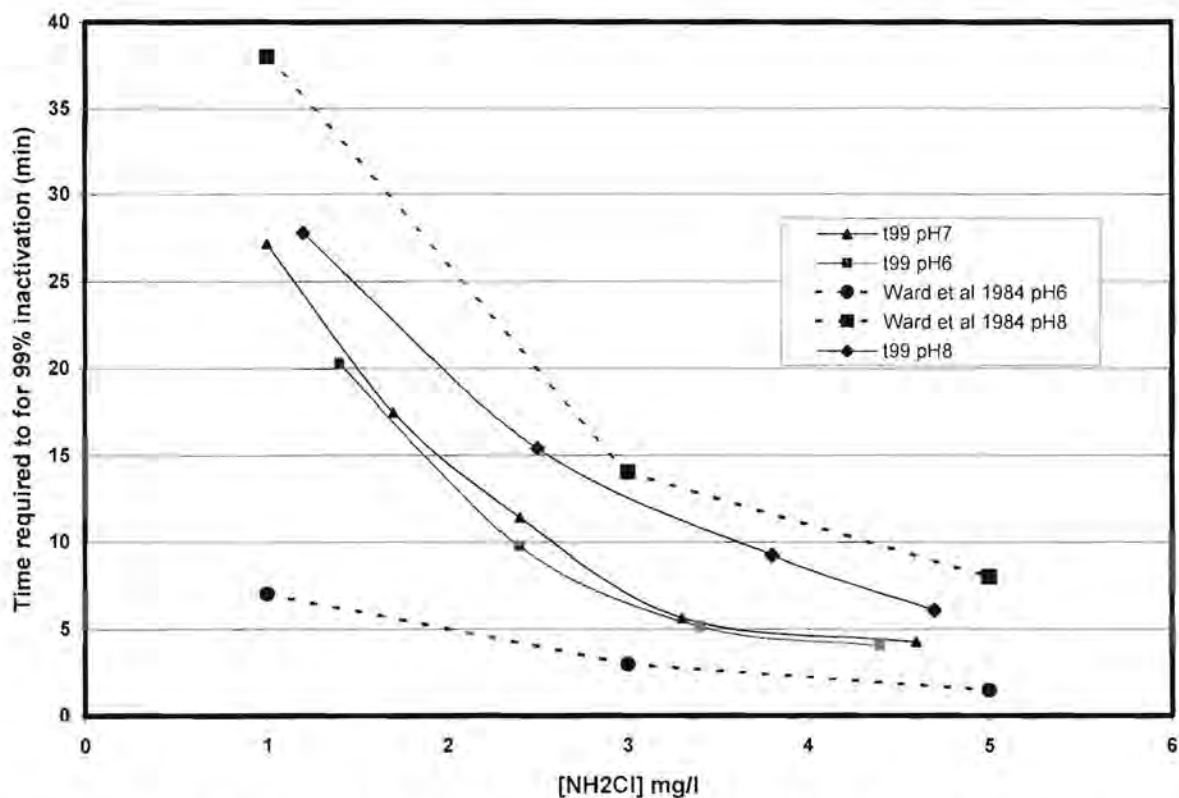


Figure 6: A comparison between the disinfection efficiency obtained in this study and that measured by Ward *et al.* (1984) at different pH values and monochloramine concentrations.

6.2 Tracer Studies

The tracer response curves for each of the two CCTs are shown in Figs. 7 and 8 respectively along with the theoretical curve for the corresponding number of theoretical CSTRs (N) obtained by analysis with the tanks-in-series-model.

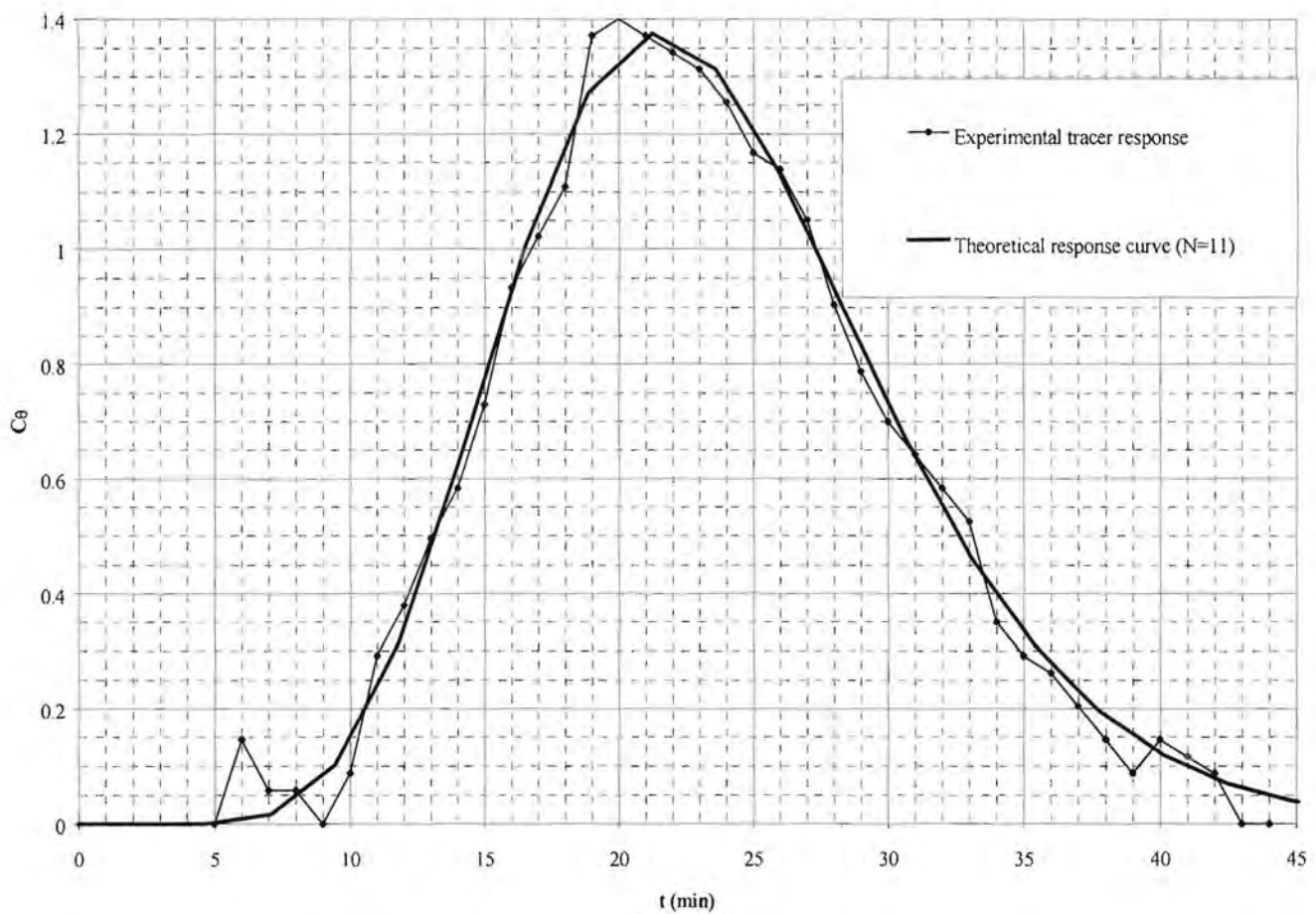


Figure 7: Experimental and theoretical tracer response curves for Reactor 1

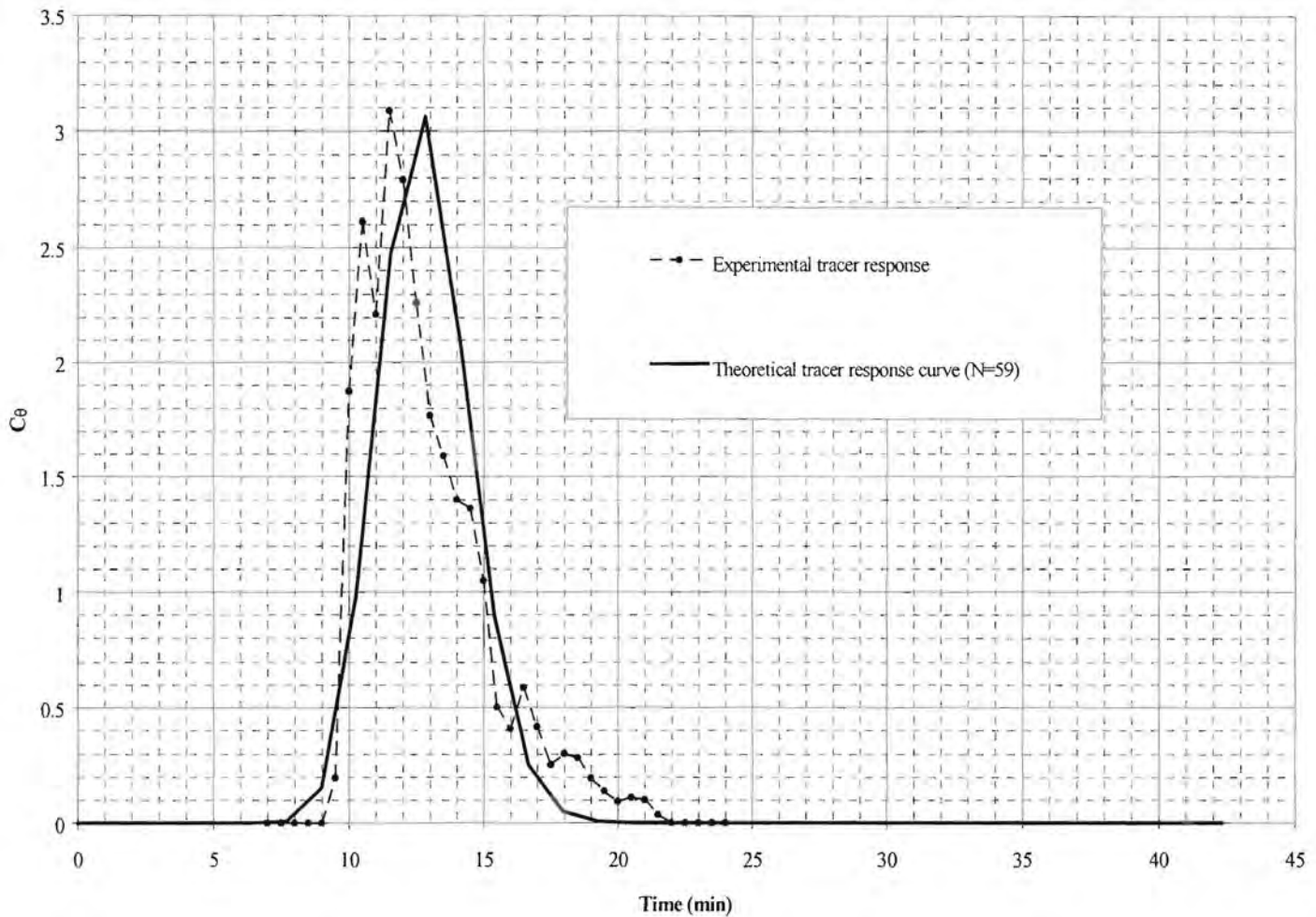


Figure 8: Theoretical and experimental tracer response curves for Reactor 2

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).

6.3 Inactivation In Continuous Flow Systems

The inactivation of faecal coliforms as measured in the continuous flow CCTs are summarised in Table 5 along with the predicted survival ratios as calculated by means of Eqn. (15). Survival ratios for Reactor 1 were predicted (Eqn. 15) 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 5: Comparison between observed and predicted inactivation in Reactor 1

Reactor 1		pH=7,39 [NH ₂ Cl] =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

Table 5 (continued): Comparison Between Observed And Predicted Inactivation In Reactor 2

Reactor 2				
Experiment	pH	[NH ₂ Cl] 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 (15) was also used to predict survival ratios for reactor 2 (N=59). As shown in Table 5 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 Figure 9.

An example of how the methodology presented in this thesis might be applied to a situation where a monochloramine disinfection system is to be retrofitted to an existing sewage treatment plant, is shown in Appendix B.

7 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 (Eqn. (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.

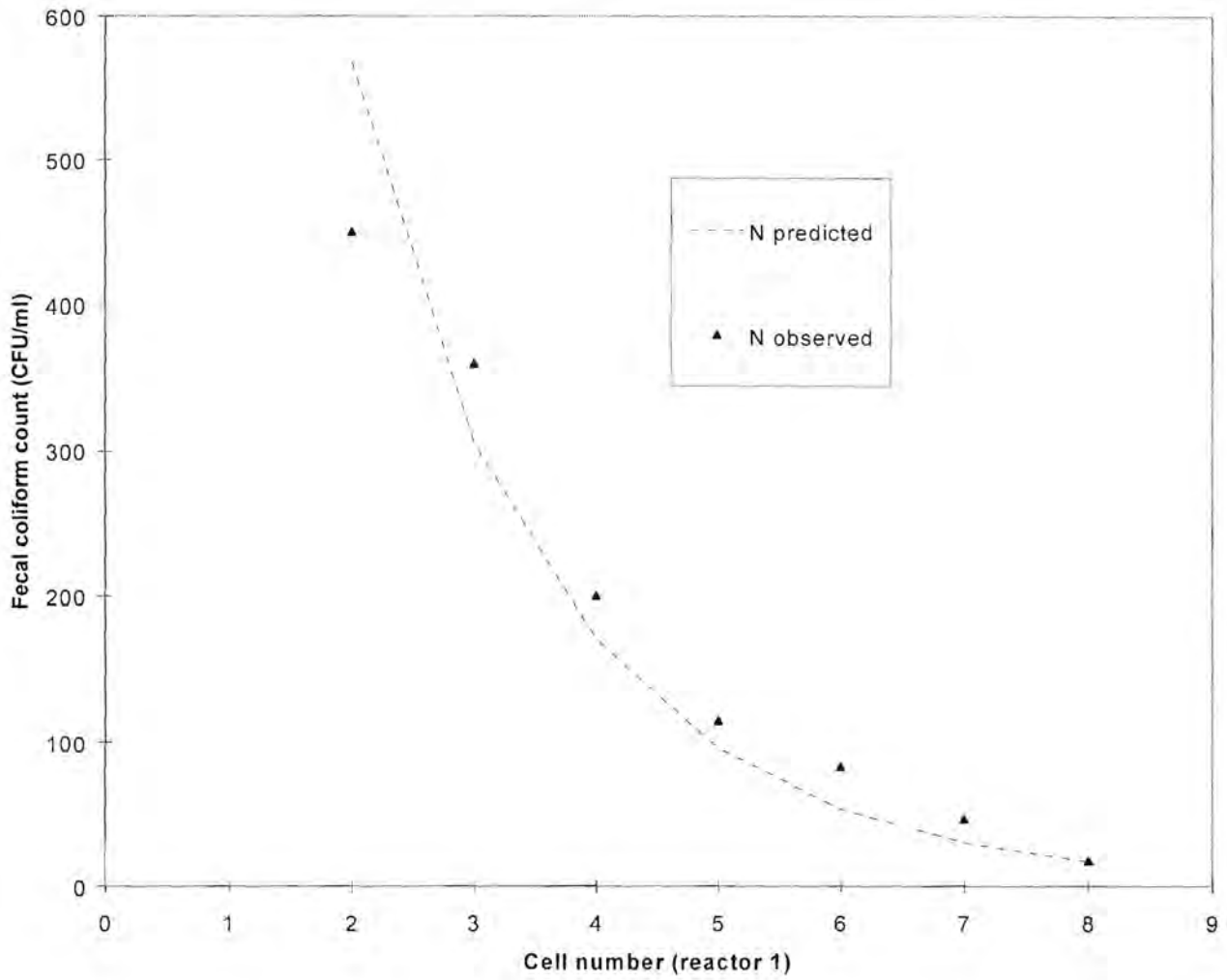


Figure 9: Evaluation of the predictive capability of Equation (15)

8 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.
- APHA (1995) Standard Methods for The Examination of Water and Waste Water. 18th Ed.
- 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*. *Canadian Journal of Microbiology* 38(1) 28-33.
- BHUPINDER SD and BAKER RA (1983) Role of ammonia-N in secondary effluent chlorination. *J. WPCF*, 55, 454
- 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.
- EKAMA GA and MARAIS GvR (1984) The nature of municipal waters. *Theory, Design and Operation of Nutrient Removal Activated Sludge Processes*, Water Research Commission, Pretoria.
- 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*.
- 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. *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*.
- TCHOBANOGLIOUS G and BURTON FL (1991) Wastewater Engineering, *McGraw-Hill, New York*. 3rd Edition.
- 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 ratio 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

A.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 were 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.

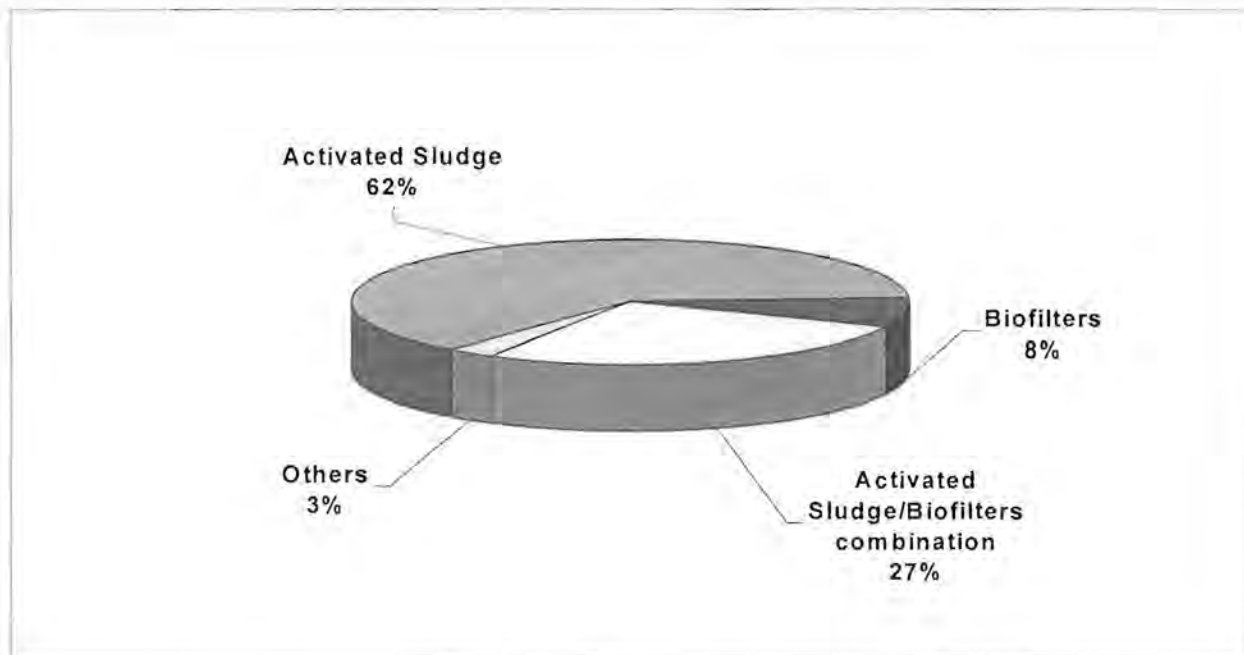


Figure A: Distribution of process type based on percentage of daily treated flow.

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.

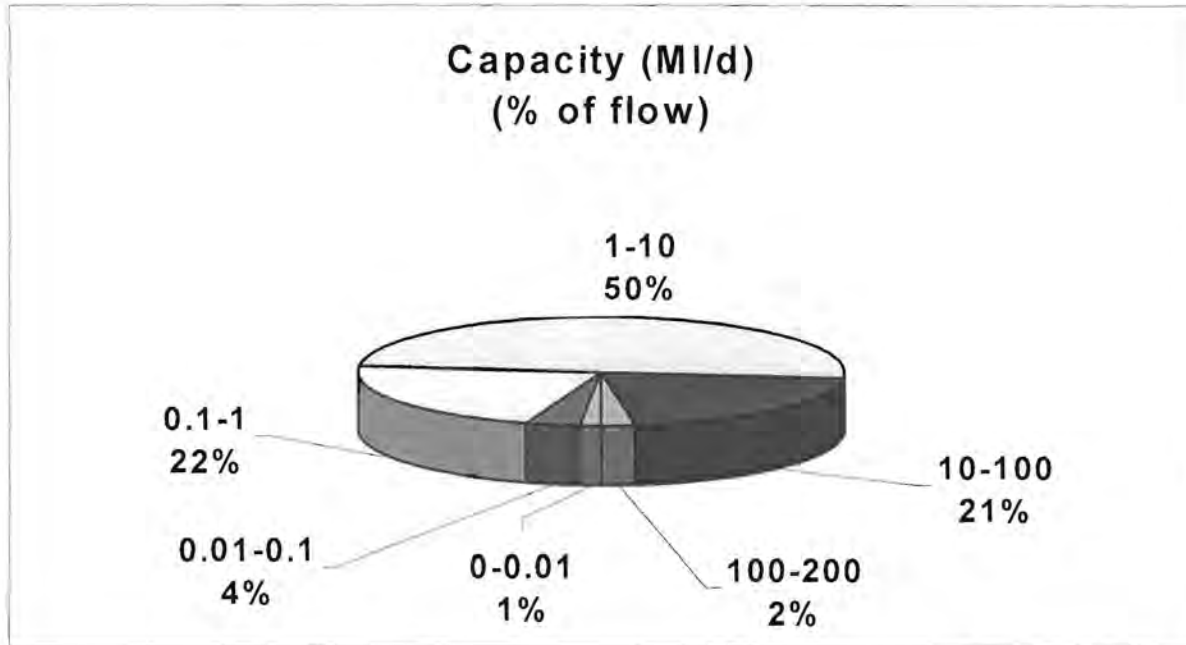


Figure B: Distribution Of The Design Capacities Of The Plants Surveyed.

A.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).

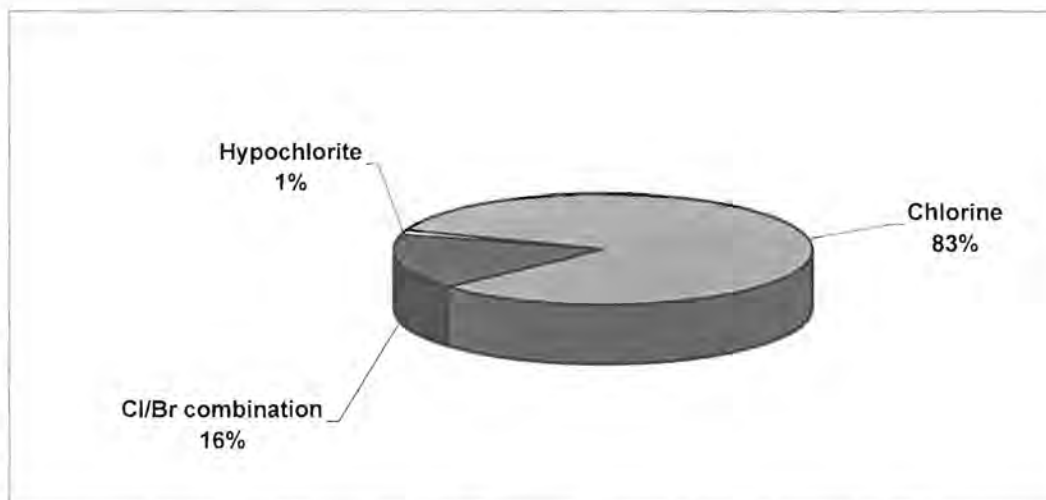


Figure C: Disinfectant Used By The Plants Surveyed Based On Total Daily Flow.

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).

A.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.

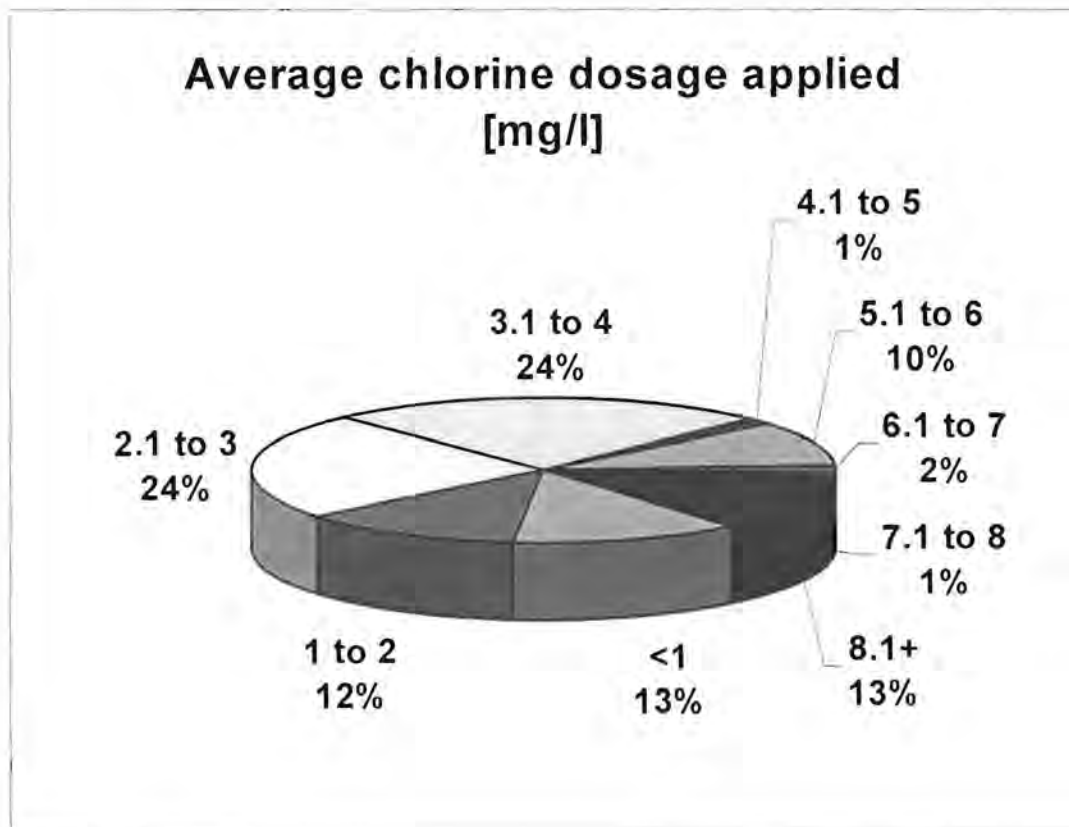


Figure D: Distribution Of Chlorine Dosages Applied Based On Total Daily Flow

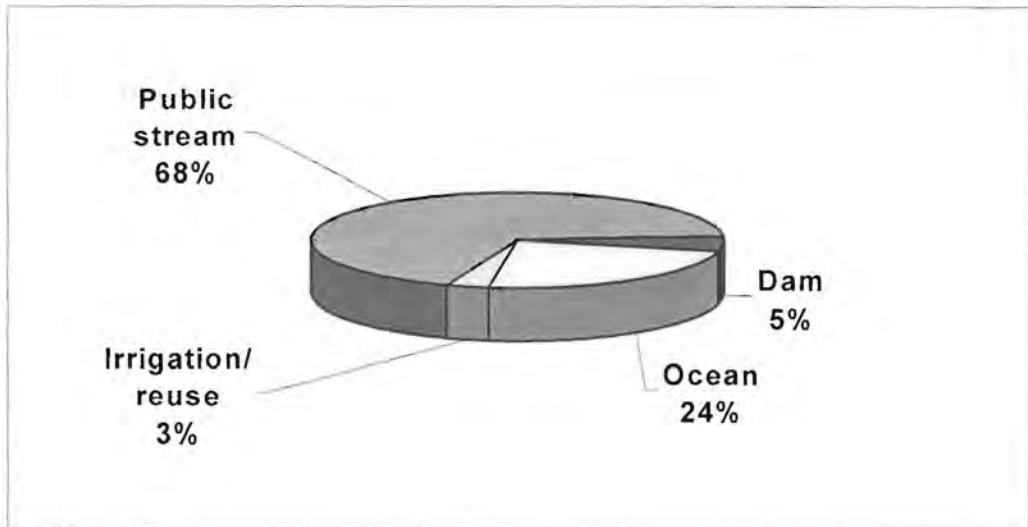


Figure E: Water Bodies Receiving The Final Effluents Of The Plants Surveyed.

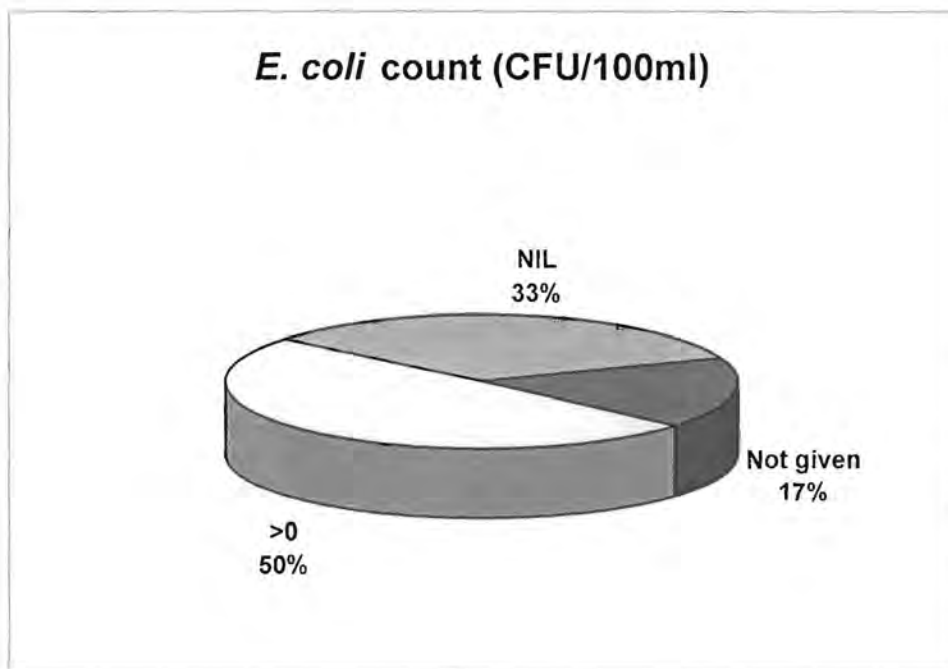


Figure F: Bacteriological Quality Of The Effluent.

A.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.

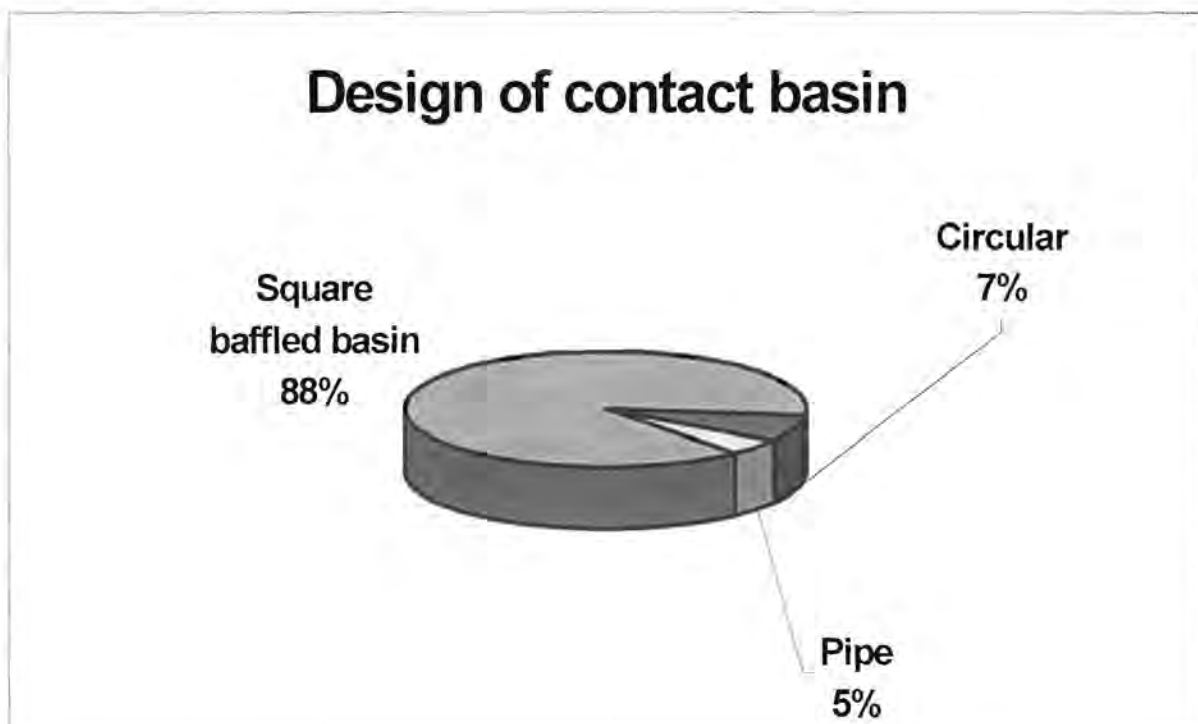


Figure G: Prevalence Of Different Contact Basin Designs.

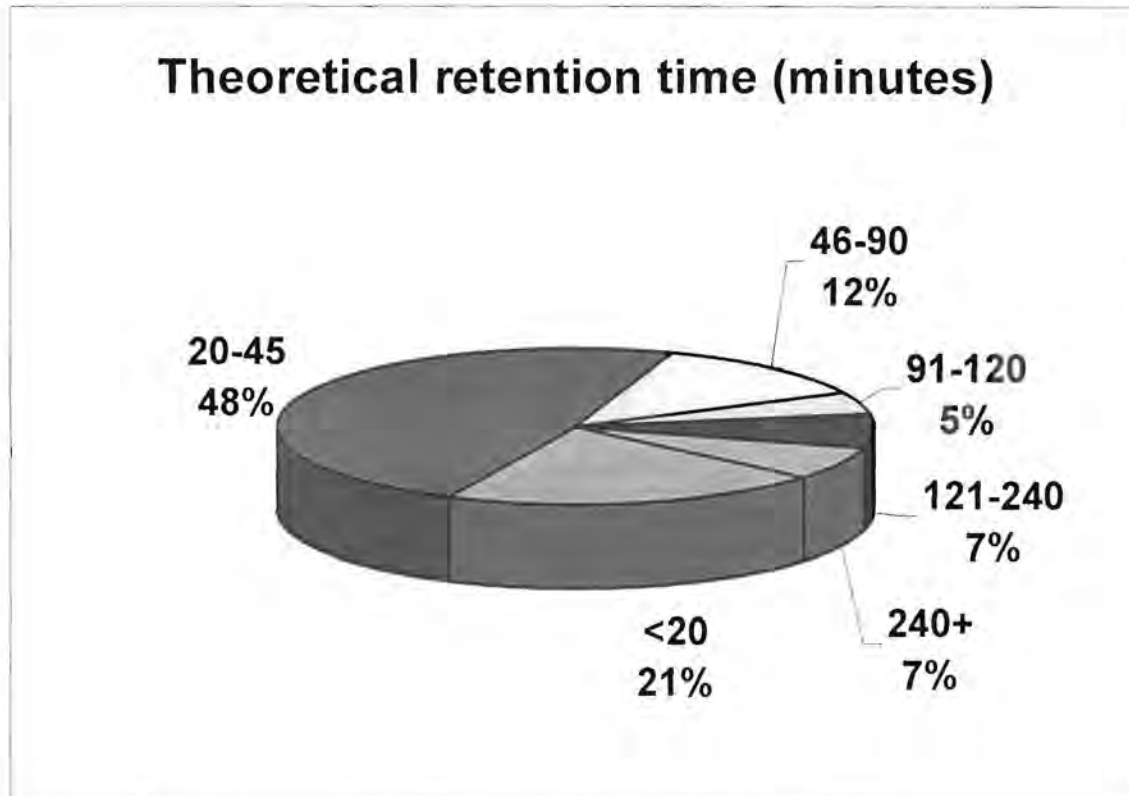


Figure H: Distribution Of Theoretical Retention Times In Contact Basins.

A.5 SUMMARY

The findings of the National Disinfection Survey can be summarised as follows:

- 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: DESIGN EXAMPLE

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

Table B1: 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 faecal coliform count	CFU/100ml	<1
Initial faecal coliform count	CFU/100ml	100 000

The objective is to determine the monochloramine concentration required to obtain a desired inactivation of faecal 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 B1:

Table B2: Data Obtained From Tracer Study.

Time (min)	Lithium concentration (mg/l)	θ	C_0	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:

$$C_{\theta} = \frac{\text{Concentration}(C)}{\text{Dose Concentration}(C_o)} \quad \text{And} \quad C_o = \frac{\text{Mass of tracer injected}}{\text{Reactor Volume}(V)}$$

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

The tracer response data is represented in Figure B.1 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:

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

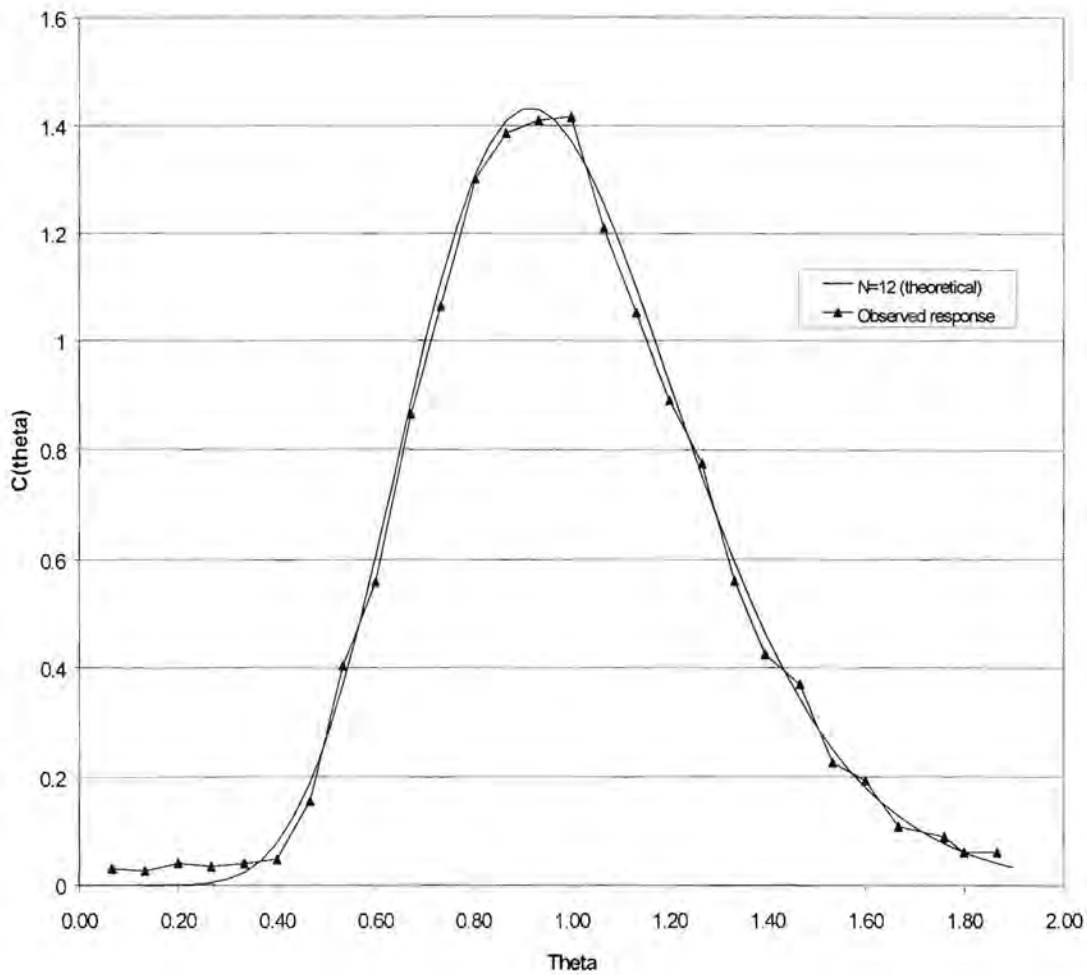


Figure B.1 Tracer Response Curve

To obtain the number of theoretical CSTR's equivalent to the CCT, the maximum value of C_{θ} , ($C_{\theta_{max}}$), 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 B2 $C_{\theta_{max}}$ 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 (15) to determine the apparent kinetic constant, K , required to obtain the desired inactivation (survival ratio):

$$\frac{N_t}{N_0} = \left(\frac{1}{1 + K\tau'} \right)^N \cdot \sum_{i=0}^{j-1} \left[\frac{i + N - 1}{N - 1} \right] \left(\frac{K\tau'}{1 + K\tau'} \right)^i \quad (\text{Equation 15})$$

Use the best fit value of $j=2$ as obtained in the experimental work reported in the main body of the thesis (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 $\tau' = 1,25$ min. Substitute the values of τ' (1,25 min), N (12) and the survival ratio, N_t/N_0 (0,0001), and calculate the corresponding value of K . The K value obtained in this way is $1,34 \text{ min}^{-1}$.

Step 4:

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